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PARTIAL OXIDATION OF BUTANE

III The Effect of Temperature, Reaction
Time and Mass Velocity

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

by

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ABSTRACT

This study is a continuation of an overall investigation of the vapour phase partial oxidation of n-butane in a flowing system. A reactor was designed and constructed which enabled a continuous measurement of reaction temperature and a limited variation of the effective reactor length.

The reaction was investigated for the effect of reaction initiation temperature - covering the range 675°F. to 750°F., of mass velocity - with the Reynolds number of the flowing gas varying from 1640 to 5340, and of reaction time - from 0.53 to 1.77 seconds. In all cases the reactor pressure was 125 p.s.i.a. and the inlet gas composition was approximately 4.0 mole % oxygen, 4.0 mole % n-butane and 92.0 mole % nitrogen.

The temperature distribution in the reactor indicates the partial oxidation reaction occupies some intermediate position between the isothermal slow oxidation of hydrocarbons and the adiabatic stationary explosions encountered in flame combustion. In all cases, where a reaction was evident, there was a pronounced induction period, followed by a relatively short period of very high reaction rates, after which the reaction died. The reaction rate showed a sharp increase between 700°F. and 725°F. The higher

temperatures reduced the induction period, increased the overall extent of the reaction and tended to form the combustion gases carbon monoxide and carbon dioxide. A decrease in mass velocity, with the reaction time constant, reduced the induction period and increased the overall extent of the reaction. The reaction products were examined for their selective formation from the reacted butane.

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INTRODUCTION

The oxidation of hydrocarbons is a complex reaction of which very little is known. Complete oxidation has been studied extensively in order to better understand the burning characteristics in internal combustion engines and in industrial furnaces. There is, however, another complete field of hydrocarbon oxidation, Partial Oxidation, which has become a major unit process for the production of organic chemicals or intermediate compounds to be used for their production. This process has been a major factor in the utilization of natural gas and the by-product condensate.

Even though the partial oxidation reaction has become a major source of many organic chemicals little data on the reaction have been published. Most publications have been confined to patent literature and qualitative descriptions of the various plants.

As a part of a series of studies on the chemical utilization of natural gas, the Research Council of Alberta and the Chemical and Petroleum Engineering Department of the University of Alberta, have been carrying out a joint research program on the partial oxidation of butane.

The work initiated in 1950 has been the subject of two Masters Theses, by R. G. Duthie and

I. Dalla Lana. The former built the original apparatus and carried out some preliminary studies (7). Dalla Lana succeeded in roughly defining the region of experimental conditions of reaction time, reactor pressure and inlet gas composition where substantial yields of oxygenated organic chemicals could be produced (5).

Dalla Lana's work showed interesting thermal effects were present during the reaction which would warrant further study. However, the study was carried out in a fixed length reactor with five fixed points where temperature measurements could be made. Consequently it was decided to build a new reactor of variable length having travelling axial thermocouples, enabling the measurement of a complete and detailed temperature distribution throughout the reaction zone.

The new reactor was designed and constructed as part of the present program. The effects of reaction initiation temperature, reaction time and mass velocity on the overall reaction were examined.

LITERATURE SURVEY

In his literature review, Dalla Lana (5) focussed his attention specifically on the partial oxidation of hydrocarbons and presented in some detail several suggested mechanisms. It is not planned here to duplicate this material but rather to survey the general field of hydrocarbon oxidation or combustion and see where partial oxidation fits into this general picture. The summary presented below is taken mainly from the books on the subject by Jost and Croft (9) and Lewis and Von Elb (11).

The oxidation of hydrocarbons has been divided into three fields, catalytic oxidation, which is self-explanatory, explosive combustion which takes place at an immeasurably fast rate, usually associated with flame fronts, and finally, slow oxidation in which the reaction rate has been suppressed to the point where it can be easily followed, normally at low temperatures (200 - 600°C.) without actual ignition taking place. A brief description will be given of each type of oxidation.

Catalytic Oxidation

With but a few exceptions, catalysts suggested for industrial use in hydrocarbon oxidation are in the

form of solids. The main reactions are consequently surface reactions and are not directly applicable to the present study. Marek and Hahn (12) discuss work where a number of compounds such as acetaldehyde, tetraethyl lead, oxides of nitrogen and hydrogen bromide have been used to study the mechanism of the oxidation reaction. However, these studies have little to do with the current work and, therefore, will not be discussed further.

Explosive Combustion

Explosive combustion can be divided into two categories: "stationary flames", where the flame remains stationary with respect to a burner and "explosive flames" where the flame front moves through the premixed gases. Stationary flames can be further divided into "diffusion flames", where the oxygen and combustible gases are mixed in the flame itself, and the "bunsen flame" where the gases are premixed before entering the combustion zone.

Diffusion flames do not represent a promising avenue of research into the combustion process since the gaseous diffusion rather than the hydrocarbon oxidation is the rate controlling step.

In a bunsen flame the actual reaction takes place in a very narrow band, a flame front, at an immeasurably fast rate. The flame front is stabilized, i.e. it becomes stationary, relative to the burner at a point where the flame velocity equals the gas velocity. This occurs near the burner exit where the gas velocity varies from its issuing velocity to nearly zero velocity some distance away. Hornbee (Lewis (11)) points out that spectrographic analysis of flames have identified the spectra of C_2 , CH, OH and CHO. The distribution of the compounds varies as the type of flame is changed.

Explosive flames spread through an available explosive mixture from a point of ignition. The study of flame propagation by Fiock and Roeder is described by Lewis (11). High speed motion pictures of the point ignition of explosive mixtures in soap bubbles revealed that the flame front travelled radially from the ignition point. However, enclosed explosions are difficult to study because of the pressure build-up and by the influence of the walls of the enclosure. Explosive combustion has little in common with the current study and as a result will not be covered further here.

Slow Oxidation

Jost (9) states that slow oxidation takes the form of an auto-catalytic reaction following a general pattern of first an "induction period", which can vary between seconds and hours depending on reaction conditions, during which no noticeable reaction takes place. The reaction rate then increases rapidly to where most of the reactants are consumed and then the reaction rate decreases. It is proposed that during the induction period some intermediate compound is formed which acts as a catalyst for the primary reaction. Once the concentration of this compound builds up the reaction rate increases until the reactants are consumed, concluding the reaction. Compounds identified in slow oxidation studies include carbon monoxide, organic acids, aldehydes, peroxides and alcohols, as well as the combustion products carbon dioxide and water.

Cool Flames

If hydrocarbons are heated in the presence of oxygen a reaction will take place at well below the ignition temperature. The reaction is recognizable by a luminescence. Prettre (Jost (9)) stated this phenomenon, known as "cool flames", has been

observed with almost all fuels except H_2 . Newman (Lewis (11)) identified aldehydes, peroxides, acids and carbon monoxide in the reaction products of a cool flame while studying a pentane-oxygen mixture.

The "cool flames" have all the characteristics of an explosive reaction but the reaction does not go to completion. The reaction is preceded by an induction period, which will vary depending on the temperature and pressure, followed by the incomplete reaction and a period of reduced reaction. Surface plays an important part in the reaction. Pease (Lewis (11)), studying the oxidation of propane showed that by filling a pyrex tube with glass chips the temperature required to initiate a reaction was increased from $375^{\circ}C$ to over $500^{\circ}C$. The condition of the surface was also shown to have an influence on the reaction. After coating the reactor with KCl no reaction took place up to $575^{\circ}C$.

Newmann (Lewis (11)) showed that an inert gas such as nitrogen has, under some conditions, an effect on the oxidation reaction. The induction period for a propane-oxygen reaction was reduced in a KCl coated pyrex reactor when nitrogen was added. No effect was noticed with a clean reactor.

The results of the studies of "slow oxidation" and "cold flames" closely resemble the results of the current studies in a dynamic system. The "flame fronts" or reaction zones established in the present studies were stabilized at a point where the flame velocity was equal to the gas velocity at a point where the residence time was equivalent to the induction period.

Recent Hydrocarbon Oxidation Studies

Skrivan and Hoelscher (18) conclude that the wall of the reactor used for their study had little effect on the oxidation of butane. They did, however, show that when the reactor was completely packed the reaction was inhibited. No diluent gas was used during this study. The paper gives a description of the five gas phase chromatographic columns used to analyze the reaction products. The product analyses were broken down into butanes, cracking reaction products and oxygenated compounds. Similar product distribution is indicated by Powers (Reidel (16)). The tendency to form each of these classifications of compounds is varied by the reaction temperature. Pressure is said to suppress the production of olefins in favor of aldehydes and ketones.

Culles, Hardy and Turner (4) have studied the point of oxygen attack on a hydrocarbon molecule using C^{14} labelled hydrocarbons. When oxidizing 2-methylpentane the initial oxygen attack favoured the 3 and 4 positions.

Allen and Long (2) also show the effect of molecular structure on the oxidation reaction. Various aldehydes are formed in changing concentration depending on the structure of the hydrocarbon molecule oxidized.

A study of slow oxidation of methane by Edgerton, Minkoff and Salooja (8) indicate a tentative reaction mechanism for the methane-oxygen reaction. The reaction product included formaldehyde, which rose through a maximum, hydrogen peroxide and hydrogen. The studies were carried out at from 440 to 520°C.

Mullen and Skirrow (15) show that the low temperature oxidation of propylene closely resembles that of the paraffin hydrocarbons.

Blundell and Skirrow (3) studied the oxidation of butane-2 in a static system. They conclude that the formation of peroxide precedes the formation of acetaldehyde, but the peroxides disappear before the reaction is completed. Inert additives (nitrogen and hydrogen) had no influence on the course of the reaction but the addition of substances occurring as intermediates (formaldehyde and acetaldehyde) showed

a pronounced effect on the reaction. Additional surface increased the induction period and reduced the amount of reaction taking place. A reaction mechanism is presented. Similar results are reported by Skirrow (17) from the study of the oxidation of hexene-1.

The studies of hydrocarbon oxidation are still incomplete. Most of the work has been conducted with only one or two variables studied, many using static conditions at near atmospheric pressure. There is little doubt that the effect of each of the major variables on the reaction changes as the other variables are changed. Further work should be done with all variables studied simultaneously.

EXPERIMENTAL PROGRAM

This phase of the study of hydrocarbon oxidation was to determine the influence of: reaction initiation temperatures, at four temperature levels 675°F., 700°F., 725°F. and 750°F., reaction times varying from approximately 0.5 to 2.0 seconds and mass velocities at Reynolds Numbers of from 1500 to 5500. The work was carried out using a constant feed composition of 4 mole % oxygen, 4 mole % butane and 92 mole % nitrogen and at a constant reactor pressure of 125 p.s.i.a.

THE REACTOR

To study the effect of reaction time with a constant mass velocity and the effect of mass velocity with a constant residence time it was necessary to use a reactor of a variable length. Such a reactor was constructed by interconnecting a series of U shaped sections of nominal $\frac{1}{4}$ inch stainless steel pipe. A schematic diagram of the reactor is shown in Figure I. The U's were connected together at the top with tees. An extension passing out of the top of the reactor bath permitted a choice of inlets to the reactor.

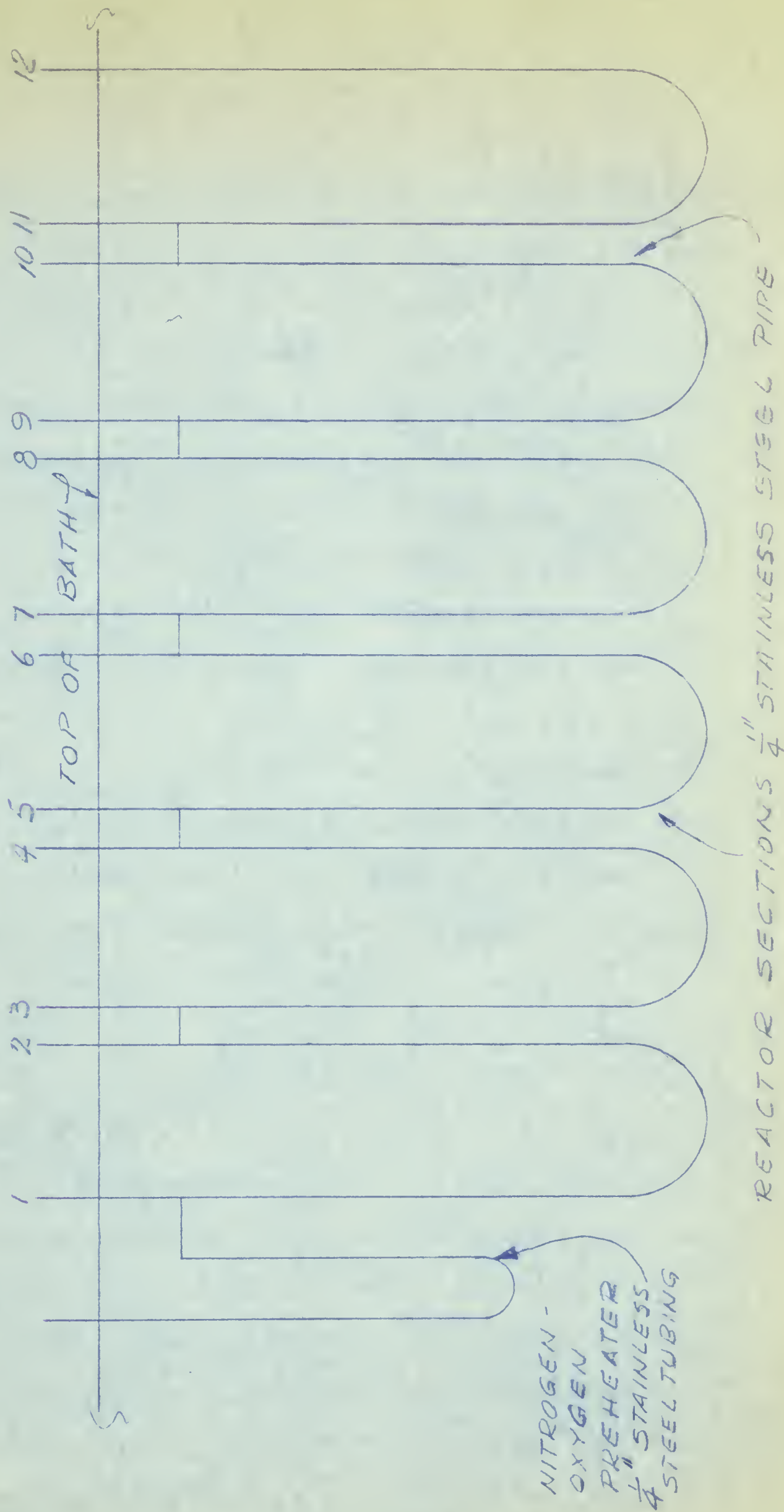


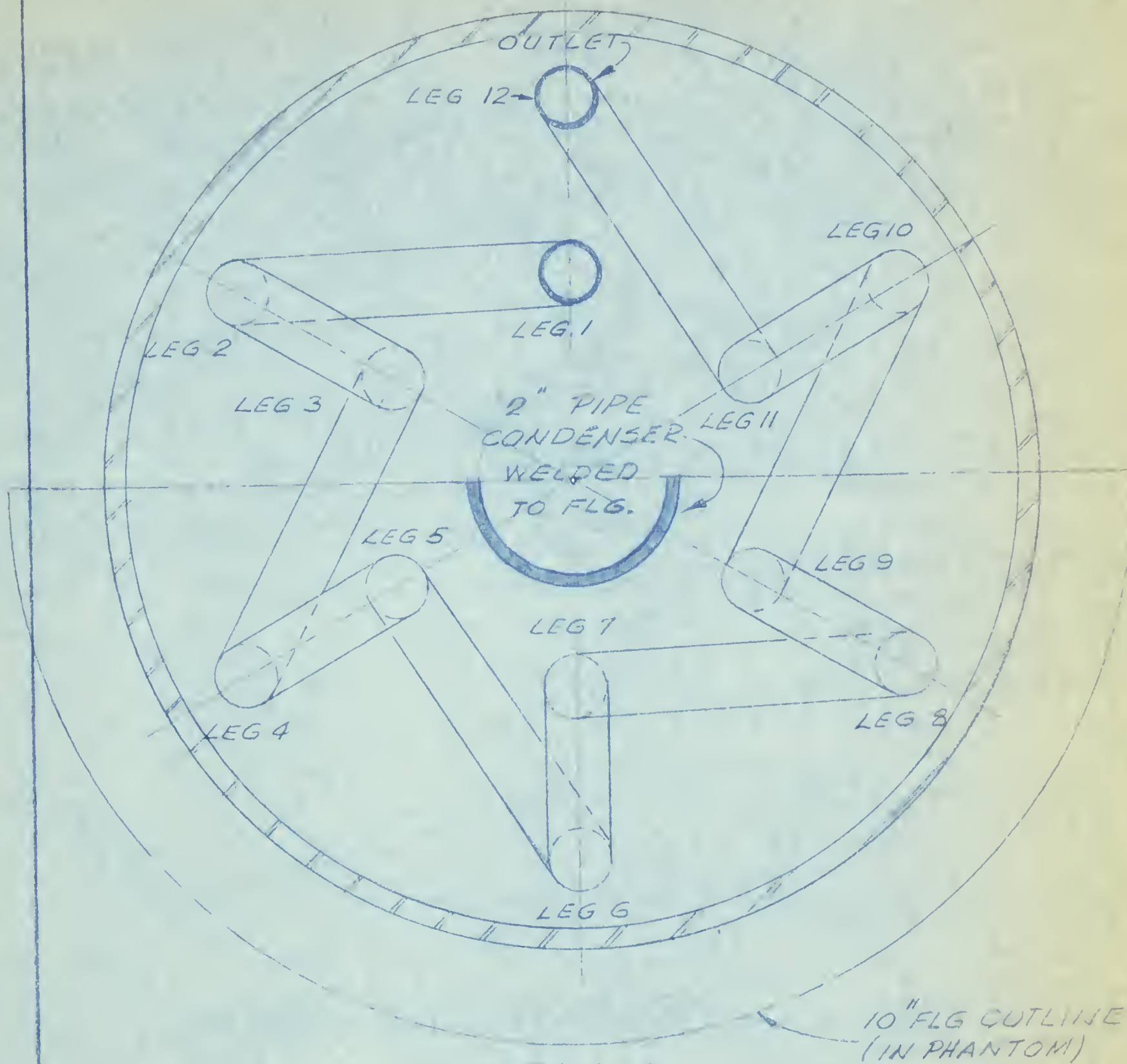
FIGURE 1
SCHEMATIC LAYOUT OF REACTOR SECTIONS

The U sections were arranged in such a fashion that they could be mounted in a standard 10 inch pipe bath. The arrangement is shown in Figure 2.

In order to measure the temperature along the reactor length axial thermowells were fitted into each of the vertical sections of the reactor. The nitrogen-oxygen mixture was preheated in a separate stainless steel tube immersed in the reactor bath. Butane was evaporated and partially preheated in a separate constant temperature bath with the final preheating taking place in an axial feed line replacing one of the thermowells mentioned above. The nitrogen-oxygen inlet was fixed but the butane inlet could be selected along the reactor depending on which thermowell was replaced. This allowed a variation in the effective reactor length.

TEMPERATURE MEASUREMENTS

Temperature measurements were taken with movable thermocouples placed in each of the thermowells. Each thermocouple could be moved to any position in the particular section of the reactor, thus allowing temperature measurements along essentially all of the reactor. Figure 3 shows the design of the thermowells and the butane feed line.



PLAN

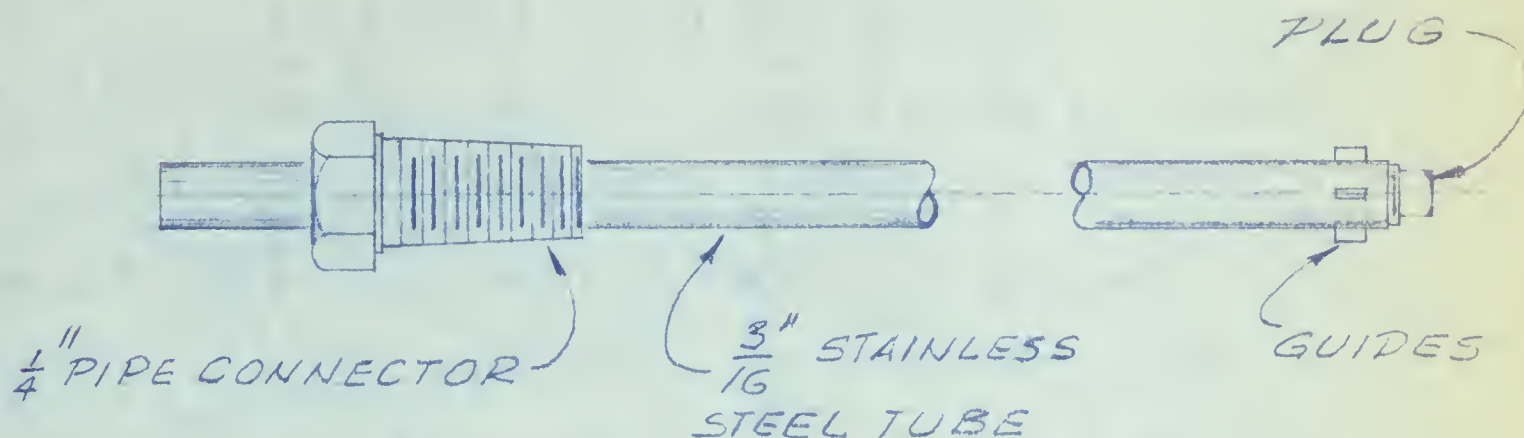
FOR REACTOR ELEVATION SEE FIG 4

FIGURE 2

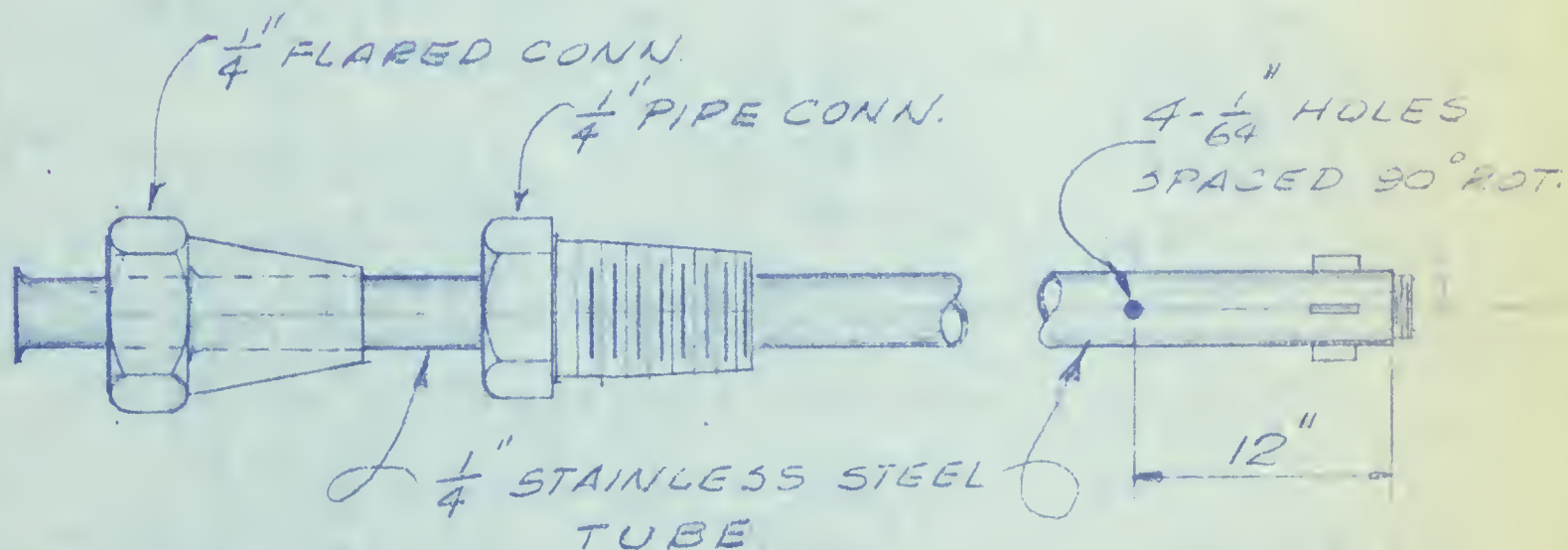
REACTOR ARRANGEMENT

FIGURE 3

THERMOWELL & BUTANE FEED
LINE DESIGNS



THERMOWELL (TYPICAL)



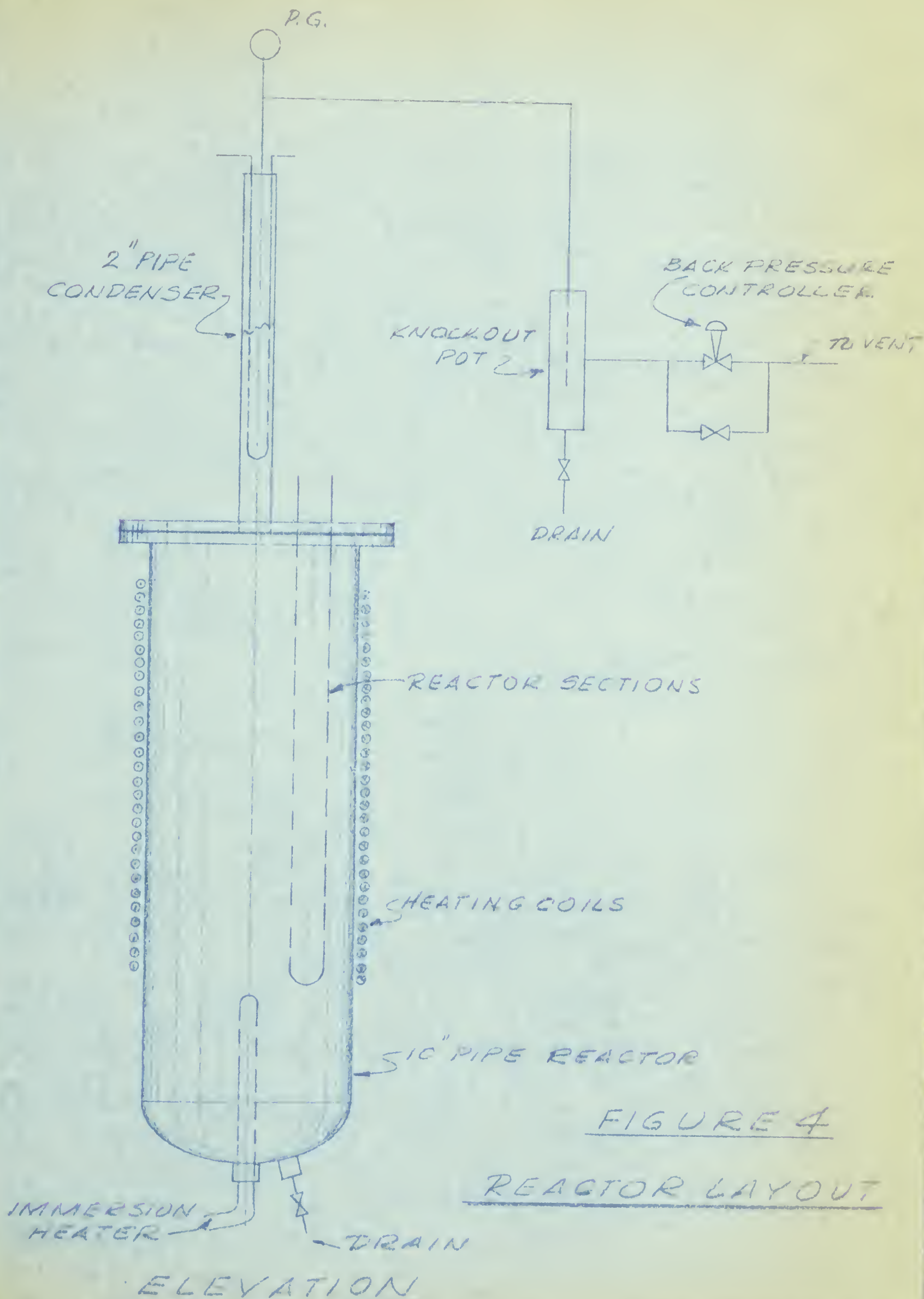
BUTANE FEED LINE

REACTOR BATH

The reaction initiation temperature was held at a constant level by immersing the reactor mentioned above in a bath of boiling Aroclor 1254 (a chlorinated biphenyl). The bath was enclosed in a section of 10 inch carbon steel pipe flanged at the top and capped at the bottom. The upper flange was fitted with a 2 inch outlet where a condenser was attached. Condensing was accomplished through the exposed surface of the pipe to the air and a U-shaped water cooled "cold finger" consisting of $\frac{1}{4}$ inch tubing inserted in the two inch pipe.

The bath temperature was controlled by maintaining a sufficiently high heat input supplied by electrical heaters, to keep the bath boiling and then adjusting the pressure on the bath to control the boiling point.

The overhead of the condenser was fitted with a back pressure valve and a bypass to relieve any pressure buildup. Figures 4 and 5 show the reactor bath. Figure 6 is a flow plan of the experimental equipment.



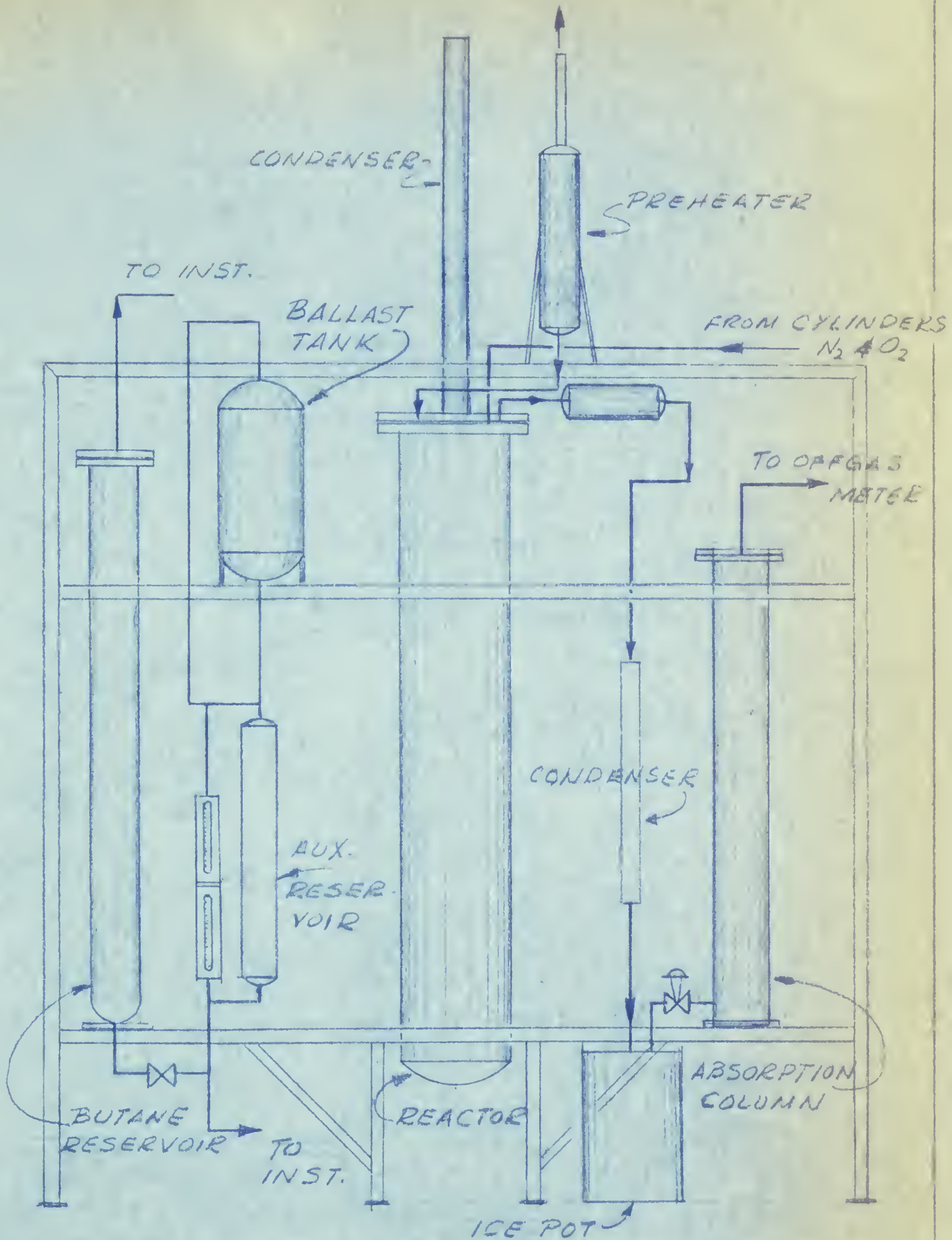


FIGURE-V
REACTOR BATH

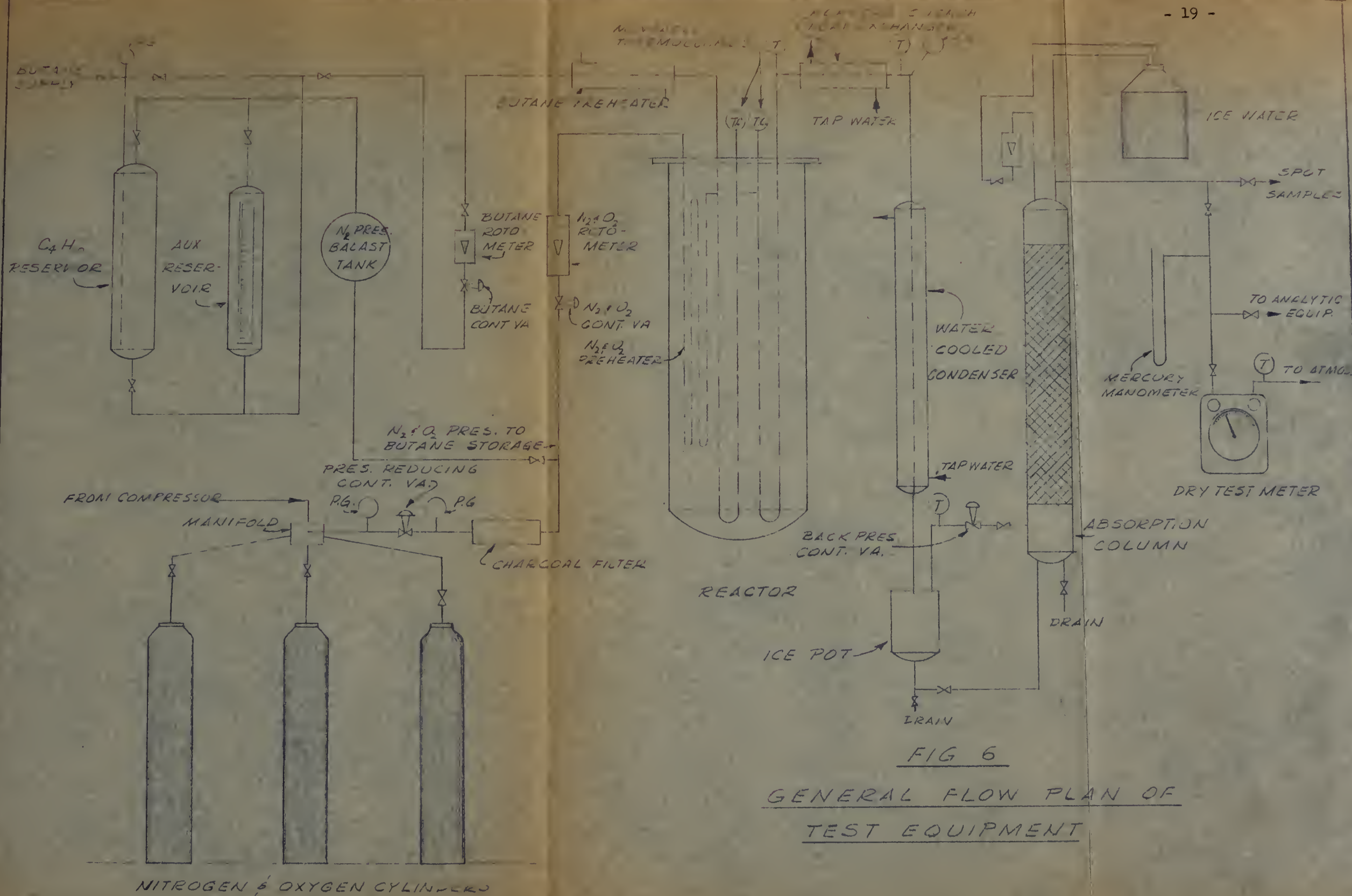


FIG 6

GENERAL FLOW PLAN OF
TEST EQUIPMENT

REACTOR HEATING

Heat was supplied to the reactor bath by a 3000 watt three way immersion heater inserted in the bottom of the bath and by two separate 2000 watt resistance windings around the bath. One of these latter heaters was always used at full load while the second was connected through a variable transformer. The bath was insulated with a two inch layer of magnesia insulation and covered with aluminum foil.

REACTION VARIABLES

Dalla Lana's work indicated that substantial yields of oxygenated organic compounds could be obtained while operating at approximately the following conditions; reaction initiation temperature 725°F., reaction time 2.0 seconds, inlet mixture 4 mole % butane, 4 mole % oxygen and 92 mole % nitrogen at a total reactor pressure of 125 p.s.i.a. The present study was to examine the influence of reaction initiation temperature at 675°F., 700°F., 725°F., and 750°F., residence time from approximately 0.5 seconds to 2.0 seconds and the effect of mass velocity at Reynolds numbers varying from approximately 1500 to 5000. The reactor pressure

was held at 125 p.s.i.a. and the inlet gas composition at 4 mole % butane, 4 mole % oxygen and 92 mole % nitrogen.

EXPERIMENTAL PROCEDURE

Preparation for Test Run

Nitrogen-Oxygen Supply

A mixture of nitrogen and oxygen of the required composition was prepared by compressing the appropriate mixture of commercial nitrogen and air. The mixture was stored in a bank of high pressure cylinders at pressures up to 2300 p.s.i.g. The cylinders were connected in parallel to a manifold which supplied the reactor. During an experimental run the nitrogen-oxygen mixture pressure was reduced from the storage pressure to about 200 p.s.i.g. with a Grove pressure reducer. This valve was found to be sufficiently sensitive to allow operation to storage pressures only slightly above that down stream from the valve with practically no variation in the down stream pressure. The mixture flow rate was controlled manually with a needle valve by holding a constant reading on a rotameter. The rotameter operated at the reactor pressure.

The required nitrogen-oxygen flow rate was determined prior to each run by setting a flow rate on the rotameter and then measuring the flow rate on the off-gas meter. Once the desired rate was obtained the rotameter reading was held constant for the remainder of the test.

Butane Supply

The butane used for the study was a Phillips blend of 99.5% n-butane. Liquid butane was transferred to reservoirs attached to the experimental equipment prior to the runs. The main reservoir consisted of a four foot length of four inch pipe. An auxiliary reservoir constructed from two inch pipe and a Jerguson sight glass served as the supply for a test run. The reservoirs were held at a constant pressure by the nitrogen-oxygen mixture at about 200 p.s.i.g.

The butane feed was metered as a liquid through a rotometer. The flow rate was held constant by manually operating a fine needle valve. Exact flow rates were obtained by measuring the butane used from the calibrated storage reservoir.

After metering the butane was vaporized and preheated before entering the reactor.

TEMPERATURE MEASUREMENT

The temperature along the reactor was measured to determine the thermal history of the reaction. The temperature measurements were taken by moving the thermocouples along the thermowells and recording the position and temperature. The temperatures were recorded with an eight point Brown recorder.

REACTION QUENCH

The reaction was quenched by passing through a double pipe heat exchanger on the reactor outlet. The gases passed through the annulus between a $\frac{1}{4}$ inch o.d. tube and a $\frac{1}{4}$ inch pipe. Cooling water ran through the inner tube. Further cooling was achieved in a second exchanger and finally in an ice bath. Liquids condensed at this point bypassed the reactor pressure controller directly to the products recovery section.

REACTOR PRESSURE CONTROL

The reactor pressure was held constant by a Grove regulator valve. This valve, a pressure reducing

regulator, was modified so that it would function as a back pressure control valve. The valve characteristics were very good over a wide range of flow rates but it was affected by changes in temperature. However, the off gas temperature was near that of the ice bath and varied very little so the reactor pressure was held very constant.

A description of the modified valve is included in the appendix.

PRODUCT ABSORPTION

The water soluble compounds in the reactor product were scrubbed from the gases in a packed absorption tower. To avoid a very dilute solution the tower was flooded at the beginning of a test and operated in that condition. The products condensed in the ice bath mentioned above were mixed with the water in the absorption tower.

The tower was completely drained at the beginning and end of each run.

OFF-GAS MEASUREMENT

The volume of off-gas was measured with a dry test meter before venting to the atmosphere. Spot

samples of the gas were taken for Orsat analysis and a side stream was drawn off for oxygen and carbon dioxide analysis in continuous gas analyzing equipment. The gas temperature was indicated on a Weston dial thermometer.

GAS ANALYSIS

The oxygen concentration in the off-gas was measured continuously with a Beckman F-3 oxygen analyzer. The carbon dioxide concentration was checked periodically with a continuous type analyzer - (one potentiometer was used for these two analyzers). The carbon dioxide analyzer is described in the appendix. The aldehyde concentration in the off-gas was measured by bubbling a metered stream of gas through a solution of 2-4, dinitrophenylhydrazine in 2N hydrochloric acid. Orsat analyses were done on spot samples for carbon dioxide, carbon monoxide, unsaturated hydrocarbons, oxygen and saturated hydrocarbons.

LIQUID ANALYSIS

The liquid collected in the absorption column during the test was weighed and stored in

a refrigerator. After all the test runs were completed samples of the liquid were sent to Consolidated Engineering in Pasadena California for mass spectrometer analysis.

EXPERIMENTAL RESULTS

Scope of the Investigation

Previous work indicated substantial yields of oxygenated hydrocarbons could be obtained operating at a reaction initiation temperature of 725°F., a reaction time of 2 seconds, a feed mixture of 4 mole % butane, 4 mole % oxygen and 92 mole % nitrogen and a pressure of 125 p.s.i.a. The present study was then set up to examine the effects of reaction initiation temperature, reaction time at constant mass velocity and constant residence time at various mass velocities. The results of these tests are reported below.

Reaction Initiation Temperature

The series of runs to measure the effect of reaction initiation temperature consisted of four runs; at 675°F., 700°F., 725°F., and 750°F. The reactions were examined for thermal effects, oxygen conversion and carbon dioxide production at the time the tests were run. In those tests where significant evidence of reaction was apparent a run was made with

appropriate gas and liquid product samples being taken. These samples were analyzed as outlined above. The analytical results were then examined for butane and oxygen conversions and selectivity of the butane to form the various product compounds. These data are presented in Tables 1, 2 and 3 and Figures 7 and 8. The temperature patterns measured through the reactor are presented as Figure 9. The test at 675°F. showed no signs of reaction; hence no reactor product samples were taken. A fifth run at 775°F. was attempted but ended when the Aroclor in the reactor bath began to decompose very rapidly making further work impossible.

The data indicates virtually no reaction at 675°F. and only slight reaction at 700°F. There is a very rapid increase in reaction rate between 700 and 725°F. Above 725°F. the reaction rate only increases slightly but there is a greater tendency to form the gaseous products CO and CO₂.

TABLE 1

The Effect of 700°F. Reaction Initiation Temperature

RUN NUMBER A-2

Feed Rate	Nitrogen-oxygen Butane	0.417 0.0150	lb. moles/hr. lb. moles/hr.	Reactor pressure 125 p.s.i.a. Reactor length 35.58 ft. Reaction temperature 700°F. Residence time 1.64 seconds Reynolds number 4760
-----------	---------------------------	-----------------	--------------------------------	---

Feed Composition

Nitrogen	92.37	mole %
Oxygen	4.16	mole %
Butane	3.47	mole %
Duration of test	29.64	minutes

Total Feed

Nitrogen	0.197	lb. moles	0.01772	lb. atoms O
Oxygen	0.00886	lb. moles	=	0.02056
Butane	0.00739	lb. moles	=	0.0739 lb. atoms H

Reactor Product⁵

Component	Moles	lb. atoms C	lb. atoms O	lb. atoms H	% of reacted carbon	% of reacted oxygen
-----------	-------	-------------	-------------	-------------	---------------------------	---------------------------

Butane ₁	0.00592	0.02368	-	0.0592	-	-
Unsats ₁	0.00085	0.00170	-	0.0034	12.2	-
Carbon monoxide	0.000426	0.000426	0.000426	-	3.0	4.9
Carbon dioxide	0.00021	0.00021	0.00042	-	1.5	4.9
Oxygen	0.00741	-	0.01482	-	-	-
Methylethyl ketone	0.000226	0.000904	0.000226	0.001808	6.4	2.6
Acetone	0.000276	0.000828	0.000276	0.001656	5.9	3.2
Other ketones ₂	0.000251	0.001255	0.000251	0.002510	8.9	2.9
Ethanol	0.000125	0.000250	0.000125	0.007500	1.8	1.4
Methanol	0.005641	0.005641	0.005641	0.022564	40.0	65.2
C ₃ and higher alcohols ₃	0.000514	0.001542	0.000514	0.004112	10.9	5.9
Acetaldehyde	0.000552	0.001104	0.000552	0.002208	7.8	6.4
Formaldehyde	0.000226	0.000226	0.000226	0.000452	1.6	2.0
Nitrogen	0.197	-	-	-	-	-
Total		0.037766	0.023477	0.09866	100.0	100.0

TABLE 1 (Continued)
The Effect of 700°F. Reaction Initiation Temperature

RUN NO. A-2

Material Balances⁶

Carbon balance	1.27
Oxygen balance	1.33
Hydrogen balance	1.34
Nitrogen balance	1.00

Conversions⁴

% of butane reacted	19.9
% of oxygen reacted	16.4

1. Unsats assumed to be ethylene
2. Other ketones assumed to be diethyl ketone
3. C₃ and higher alcohols assumed to be propanol
4. Conversions based on feed and unreacted component out
5. Oxygen balance and % of reacted oxygen do not include any oxygen in product as H₂O.
6. Off gas meter not read. Product based on N₂ balance.

TABLE 2
The Effect of 725°F. Reaction Initiation Temperature

RUN NUMBER A-3		Nitrogen-oxygen		0.372		lb. moles/hr.		Reactor Pressure		125 p.s.i.a.	
Feed Rate		Butane		0.0162		lb. moles/hr.		Reactor length		38.58 ft.	
Feed Composition		Nitrogen		91.81		mole %		Reaction temperature		725°F.	
		Oxygen		4.02		mole %		Residence time		1.77 seconds	
		Butane		4.17		mole %		Reynolds Number		4230	
Duration of Test		53.1		minutes							
Total Feed Nitrogen		0.308		lb. moles							
Oxygen		0.01345		lb. moles		=		lb. atoms		0	
Butane		0.01397		lb. moles		=		lb. atoms C and		0.1397 lb. atoms	
Reactor Product ⁵											
Component		Moles		lb. atoms carbon		lb. atoms oxygen		% of reacted carbon		% of reacted oxygen	
Butane ₁		0.00912		0.03648		-		-		-	
Unsats ₁		0.00137		0.00274		-		11.2		-	
Carbon monoxide		0.00366		0.00366		0.00366		15.0		21.5	
Carbon dioxide		0.00155		0.00155		0.00310		6.3		18.1	
Oxygen		0.00421		-		0.00842		-		-	
Methylethyl ketone		0.000394		0.001576		0.000394		6.4		2.3	
Acetone		0.000036		0.000108		0.000036		0.4		0.2	
Other ketones ²		0.000251		0.001255		0.000251		5.1		1.5	
Ethanol		0.000107		0.000214		0.000107		0.9		0.6	
Methanol		0.005214		0.005214		0.005214		21.3		30.8	
C ₃ and higher											
Alcohols ³		0.001254		0.003762		0.001254		15.4		7.3	
Acetaldehyde		0.001397		0.002794		0.001397		11.3		8.2	
Formaldehyde		0.001648		0.001648		0.001648		6.7		9.7	
Nitrogen		0.3065		-		-		-		-	
Total				0.061003		0.02549		100.0		100.0	

TABLE 2 (Continued)
The Effect of 725°F. Reaction Initiation Temperature

RUN NUMBER A-3

Material balances		
Carbon balance	1.09	
Oxygen balance	0.947	
Hydrogen balance	1.04	
Nitrogen balance	0.996	
Conversion ⁴		
% butane reacted	34.7	
% oxygen reacted	68.6	

1. Unsats assumed to be ethylene
2. Other ketones assumed to be diethyl ketone
3. C₃ and higher alcohols assumed to be propanol
4. Conversions based on feed and unreacted component out
5. Oxygen balance and % of reacted oxygen do not include any oxygen in product as H₂O.

TABLE 3

The Effect of 750°F. Reaction Initiation Temperature

RUN NUMBER A-4

Feed Rate	Nitrogen-oxygen Butane	0.364 0.0155	lb. moles/hr. lb. moles/hr.	Reactor Pressure Reactor Length Reaction temperature Residence time Reynolds Number	125 p.s.i.a. 35.58 ft. 750°F. 1.77 seconds 4120
Feed Composition	Nitrogen Oxygen Butane	91.95 3.98 4.07	mole % mole % mole %		
Duration of test		63.93	minutes		
Total Feed Nitrogen		0.371	lb. moles		
Oxygen		0.0161	lb. moles	0.0322 lb. atoms oxygen	
Butane		0.0159	lb. moles	0.0637 lb. atoms carbon and 0.1590 lb. atoms H	

Reactor Product⁵

Component	Moles	lb. atoms carbon	lb. atoms oxygen	lb. atoms hydrogen	% of reacted carbon	% of reacted Oxygen
Butane ¹	0.01063	0.04252	-	0.1063	-	-
Unsats ¹	0.00238	0.00476	-	0.00952	23.5	-
Carbon monoxide	0.00455	0.00455	0.00455	-	22.4	31.3
Carbon dioxide	0.00273	0.00273	0.00546	-	13.5	37.4
Oxygen	0.00382	-	0.00764	-	-	-
Methylethyl ketone	0.000248	0.001136	0.000284	0.002272	5.6	2.0
Acetone	-	-	-	-	-	-
Other ketones ²	0.000158	0.000790	0.000158	0.001580	3.9	1.1
Ethanol	0.000063	0.000126	0.000063	0.000378	0.6	0.4
Methanol	0.001609	0.001609	0.001609	0.006436	8.0	11.0
C ₃ and higher ³						
alcohols ³	0.000820	0.002460	0.000820	0.006560	12.2	5.6
Acetaldehyde	0.000442	0.000884	0.000442	0.001768	4.4	3.0
Formaldehyde	0.001199	0.001199	0.001199	0.002398	5.9	8.2
Nitrogen	0.375	-	-	-	-	-
Total		0.062759	0.022221	0.137212	100.0	100.0

TABLE 3 (Continued)
The Effect of 750°F. Reaction Initiation Temperature

RUN NUMBER A-4

Material Balances

Carbon balance	0.985
Oxygen balance	0.69
Hydrogen balance	0.86
Nitrogen balance	1.01

Conversion⁴

% butane reacted	32.3
% oxygen reacted	75.6

1. Unsats assumed to be ethylene
2. Other ketones assumed to be diethyl ketone
3. C₃ and higher alcohols assumed to be propanol
4. Conversions based on feed and unreacted component out
5. Oxygen balance and % of reacted oxygen do not include any oxygen in product as H₂O.

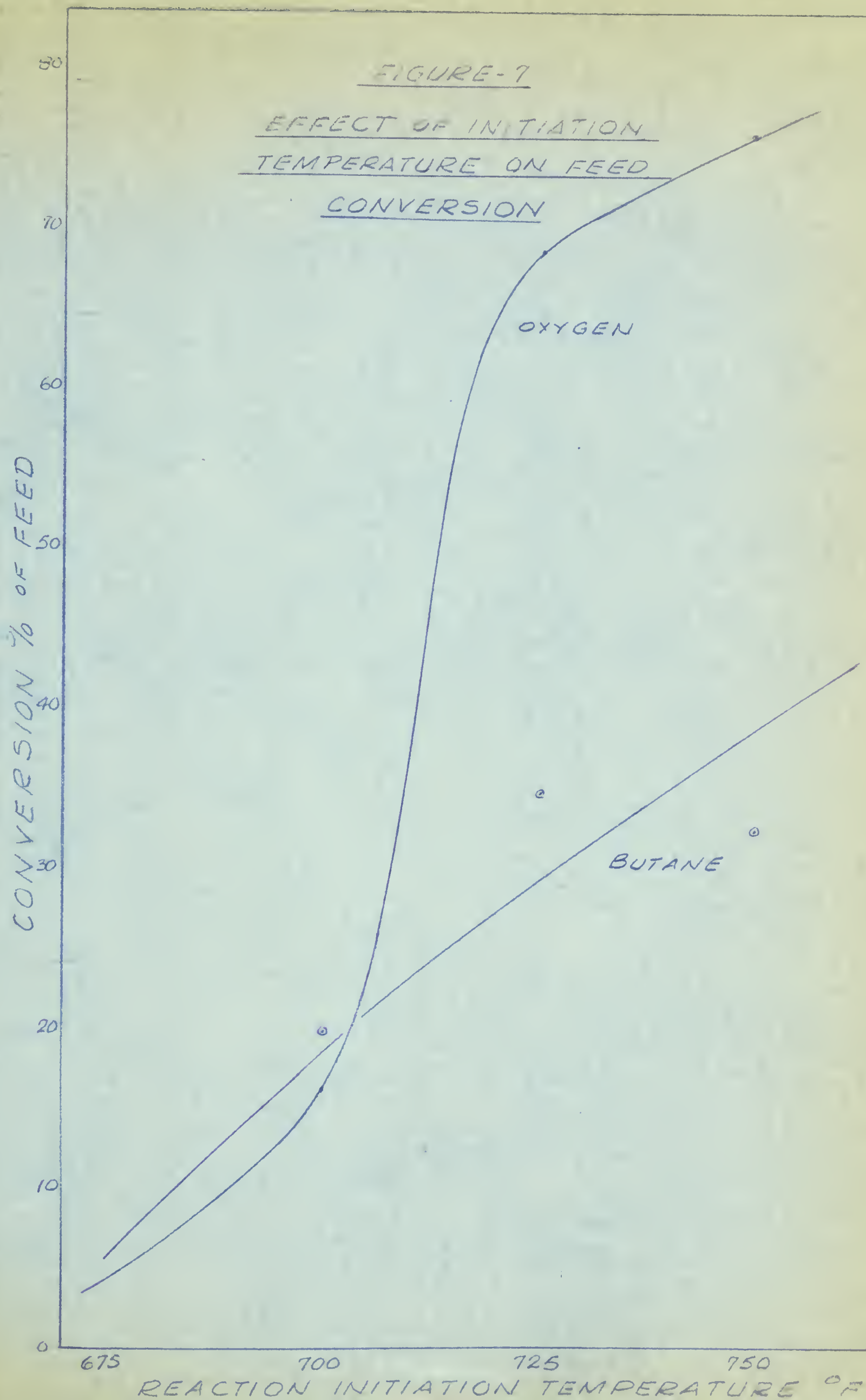


FIGURE 8

THE EFFECT OF REACTION INITIATION

TEMPERATURE ON BUTANE SELECTIVITY

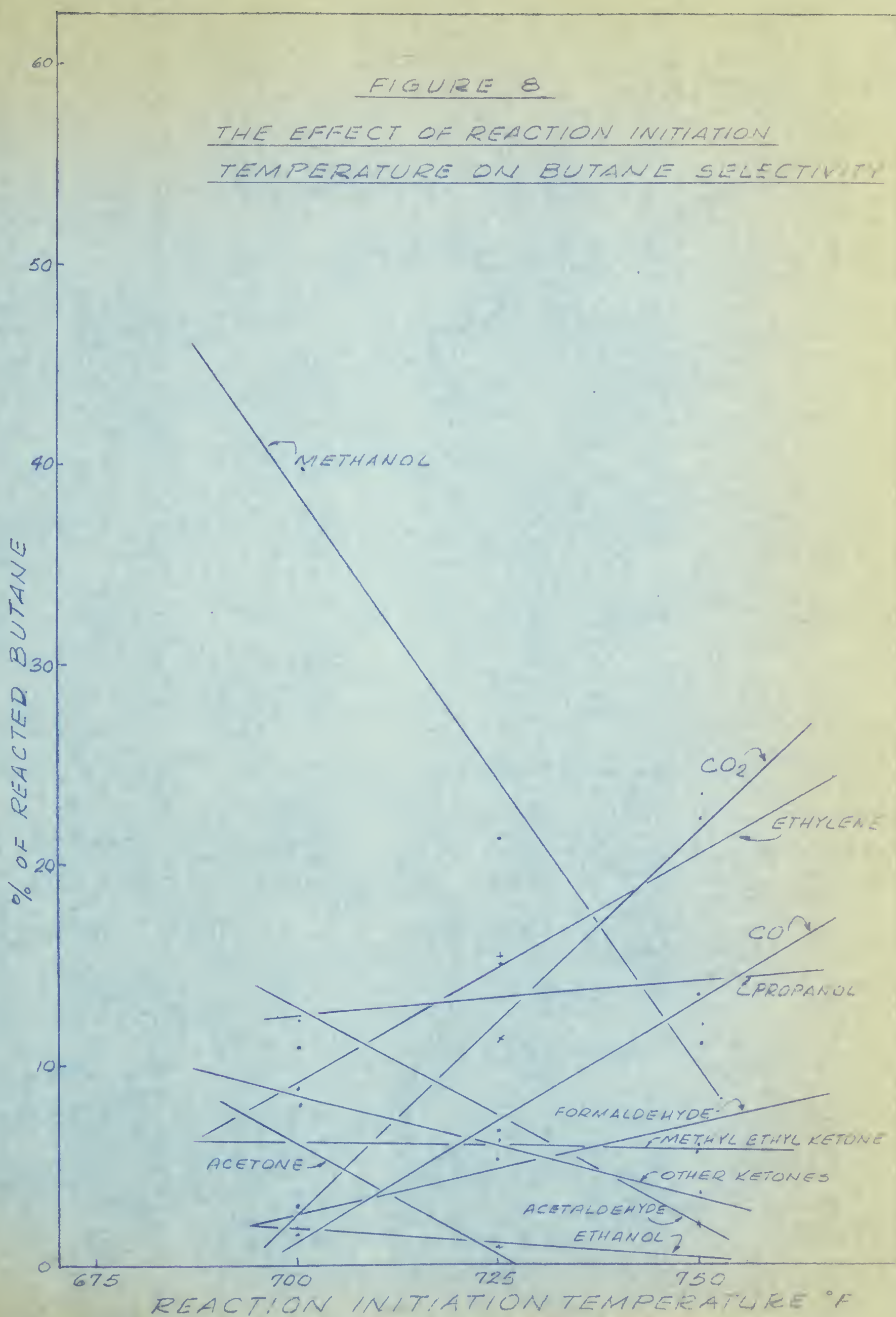
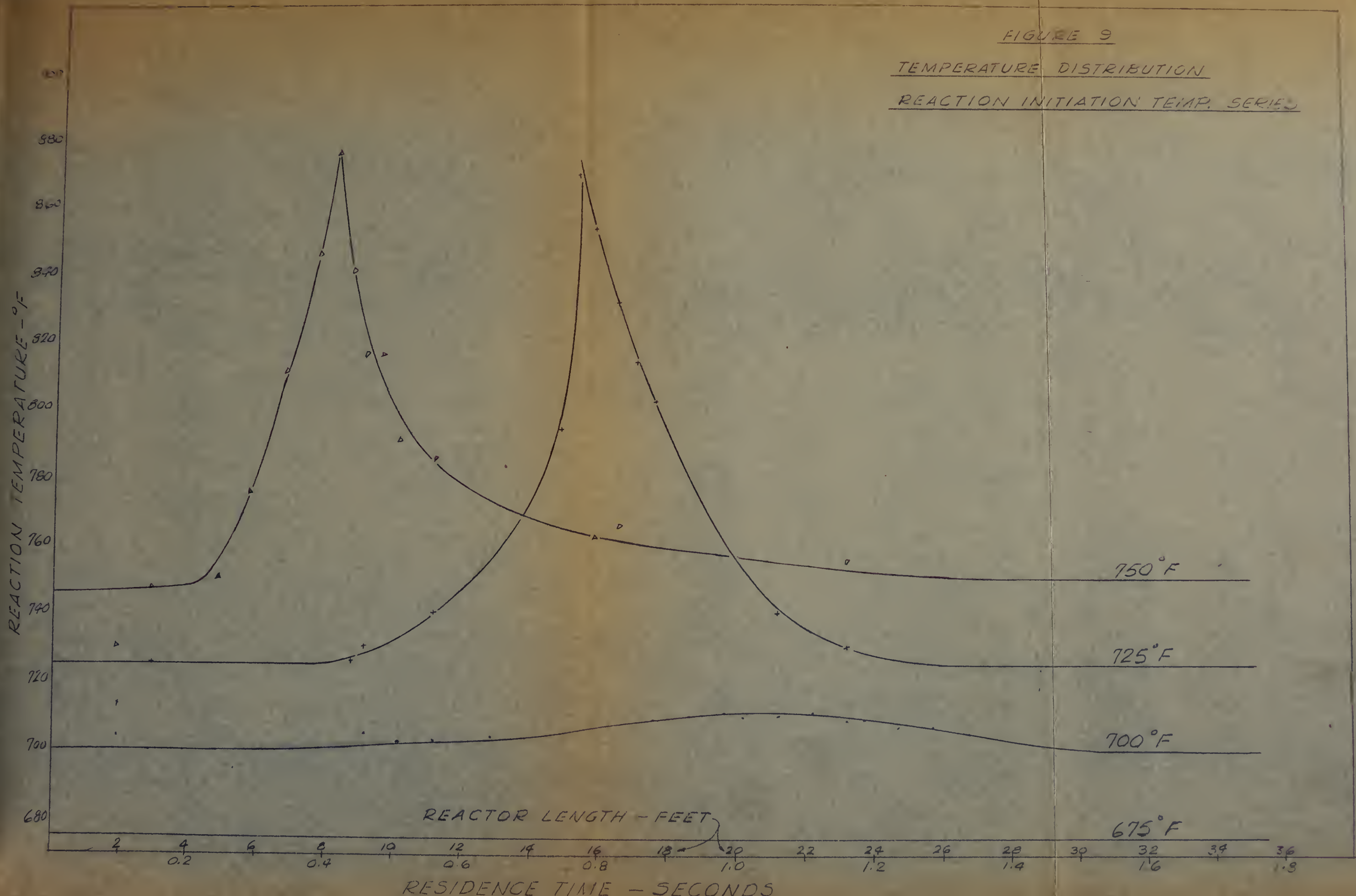


FIGURE 9
TEMPERATURE DISTRIBUTION
REACTION INITIATION TEMP. SERIES



Residence Time

The series of tests at various residence times was accomplished by injecting the butane feed at various points along the reactor. The flow rates and reaction initiation temperatures were held constant during these tests. Residence times used were: 1.77, 1.28, 1.03, 0.906, 0.664 and 0.533 seconds. Oxygen analysis and temperature measurements indicated appreciable reaction was taking place at all but 0.533 seconds. With the exception of this one run, gas and liquid samples were taken for analyses and product work-ups. These data are presented as Tables 4, 5, 6, 7 and 8 and Figures 10 and 11. A plot of the temperature distribution for this series of runs is presented as Figure 12. It can be seen that there was very little reaction taking place during the first 0.3 seconds after the feed was introduced into the reactor. The rate of reaction began to increase after 0.3 seconds, becoming extremely rapid between 0.6 and 0.7 seconds residence time. The reaction product temperature follows a near adiabatic cooling curve after 0.7 seconds, indicating very little reaction took

TABLE 4
The Effect of 1.77 Second Residence Time

RUN NUMBER B-1 (as A-3)

Feed Rate	Nitrogen-oxygen Butane	0.372 0.0162	lb. moles/hr. lb. moles/hr.	Reactor Pressure 125 p.s.i.a. Reactor length 38.58 ft. Reaction temperature 725°F. Residence time 1.77 seconds Reynolds Number 4230
Feed Composition	Nitrogen Oxygen Butane	91.81 4.02 4.17 53.1	mole % mole % mole % minutes	
Duration of Test		0.308	lb. moles	
Total Feed Nitrogen	Oxygen	0.01345	lb. moles =	0.02690 lb. atoms O
	Butane	0.01397	lb. moles =	0.05588 lb. atoms C and 0.1397 lb. atoms H
Reactor Product ⁵				

Component	Moles	lb. atoms carbon	lb. atoms oxygen	lb. atoms hydrogen	% of reacted carbon	% of reacted oxygen
Butane ¹	0.00912	0.03648	-	0.0912	-	-
Unsats	0.00137	0.00274	-	0.00548	11.2	-
Carbon monoxide	0.00366	0.00366	0.00366	-	15.0	21.5
Carbon dioxide	0.00155	0.00155	0.00310	-	6.3	18.1
Oxygen	0.00421	-	0.00842	-	-	-
Methylethyl ketone	0.000394	0.001576	0.000394	0.003153	6.4	2.3
Acetone	0.000036	0.000108	0.000036	0.000216	0.4	0.2
Other ketones ²	0.000251	0.001255	0.000251	0.002510	5.1	1.5
Ethanol	0.000107	0.000214	0.000107	0.000642	0.9	0.6
Methanol	0.005214	0.005214	0.005214	0.020856	21.3	30.8
C ₃ and higher ³						
alcohols	0.001254	0.003762	0.001254	0.012032	15.4	7.3
Acetaldehyde	0.001397	0.002794	0.001397	0.005588	11.3	8.2
Formaldehyde	0.001648	0.001648	0.001648	0.003926	6.7	9.7
Nitrogen	0.3065	-	-	-	-	-
Total		0.061003	0.02549	0.14497	100.0	100.0

TABLE 4 (Continued)
The Effect of 1.77 Second Residence Time

RUN NUMBER B-1 (as A-3)

Material balances

Carbon balance	1.09
Oxygen balance	0.947
Hydrogen balance	1.04
Nitrogen balance	0.996

Conversion⁴

% of butane reacted	34.7
% of oxygen reacted	68.6

1. Unsats assumed to be ethylene
2. Other ketones assumed to be diethyl ketone
3. C₃ and higher alcohols assumed to be propanol
4. Conversions based on feed and unreacted component out
5. Oxygen balance and % of reacted oxygen do not include any oxygen in product as H₂O.

TABLE 5
The Effect of 1.28 Seconds Residence Time

RUN NUMBER B-2

Feed Rate Nitrogen-oxygen	0.372	lb. moles/hr.	Reactor pressure 125 p.s.i.a.
Butane	0.0157	lb. moles/hr.	Reactor length 25.39 ft.
Feed Composition			Reactor temperature 725°F.
Nitrogen	91.97	mole %	Residence time 1.28 seconds
Oxygen	3.98	mole %	Reynolds Number 4230
Butane	4.05	mole %	
Duration of Test	57.62	minutes	
Total Feed Nitrogen	0.342	lb. moles	
Oxygen	0.0149	lb. moles = 0.02970	lb. atoms 0
Butane	0.015024	lb. moles = 0.060096	lb. atoms C and 0.15024 lb. atoms H
Reactor Product ⁵			
Component	Moles	lb. atoms Carbon	lb. atoms Hydrogen
Butane ¹	0.00938	0.037520	0.0938
Unsats	0.00158	0.00316	0.00632
Carbon monoxide	0.00286	0.00286	-
Carbon dioxide	0.00240	0.00240	-
Oxygen	0.00533	-	-
Methylethyl ketone	0.000330	0.001320	0.002640
Acetone ²	0.000030	0.000090	0.000180
Other ketones	0.000150	0.000750	0.00150
Ethanol	0.000090	0.000180	0.000540
Methanol	0.001439	0.001439	0.005756
C ₃ and higher ³			
alcohols	0.000870	0.002610	0.006960
Acetaldehyde	0.000570	0.001140	0.002280
Formaldehyde	0.000660	0.000660	0.001320
Nitrogen	0.325	-	-
Total		0.054129	0.12130
		0.022459	100.0
			100.0
			24.2
			40.6
			-
			2.8
			0.3
			1.3
			0.8
			12.2
			7.4
			4.8
			5.6
			-
			15.7
			6.9
			4.0
			-
			100.0
			100.0

TABLE 5 (Continued) —
The Effect of 1.28 Seconds Residence Time

RUN NUMBER B-2

Material Balances

Carbon balance	0.900
Oxygen balance	0.758
Hydrogen balance	0.810
Nitrogen balance	0.952

Conversion⁴

% of butane reacted	37.6
% of oxygen reacted	65.3

1. Unsats assumed to be ethylene
2. Other ketones assumed to be diethyl ketone
3. C₃ and higher alcohols assumed to be propanol
4. Conversions based on feed and unreacted component out
5. Oxygen balance and % of reacted oxygen do not include any oxygen in product as H₂O.

TABLE 6
The Effect of 1.03 Seconds Residence Time

RUN NUMBER B-3

Feed Rate Nitrogen-oxygen	0.372	lb. moles/hr.	Reactor Pressure	125 p.s.i.a.
Butane	0.0148	lb. moles/hr.	Reactor length	20.79 ft.
Feed Composition			Reaction temperature	725°F.
Nitrogen	92.21	mole %	Residence time	1.03 seconds
Oxygen	3.96	mole %	Reynolds Number	4220.
Butane	3.83	mole %		
Duration of Test	33.67	minutes		
Total Feed Nitrogen	0.200	lb. moles		
Oxygen	0.00860	lb. moles		
Butane	0.00829	lb. moles		

Reactor Product⁵

Component	Moles	lb. atoms Carbon	lb. atoms Oxygen	lb. atoms Hydrogen	% of reacted Carbon	% of reacted oxygen
Butane ₁	0.00518	0.02072	-	0.0518	-	-
Unsats	0.000975	0.00195	-	0.0039	11.7	-
Carbon monoxide	0.002552	0.002552	0.002552	-	15.2	19.3
Carbon dioxide	0.001617	0.001617	0.003214	-	9.7	24.3
Oxygen	0.003604	-	0.007208	-	-	-
Methylethyl ketone	0.000209	0.000836	0.000209	0.01672	5.0	1.6
Acetone	-	-	-	-	-	-
Other ketones ²	0.000175	0.000875	0.000175	0.00175	5.2	1.3
Ethanol	0.000105	0.000210	0.000105	0.000630	1.3	0.8
Methanol	0.001501	0.001501	0.001501	0.006004	9.0	11.4
C ₃ and higher ³	0.000768	0.002304	0.000768	0.006134	13.7	5.8
alcohols	0.000244	0.000488	0.000244	0.000976	2.9	1.9
Acetaldehyde	0.004398	0.004398	0.004398	0.008796	26.3	33.4
Formaldehyde	0.205	-	-	-	-	-
Nitrogen						
Total		0.037451	0.013186	0.08146	100.0	100.0

TABLE 6 (Continued)
The Effect of 1.03 Seconds Residence Time

RUN NUMBER B-3

Material Balances

Carbon balance	1.13
Oxygen balance	1.19
Hydrogen balance	0.985
Nitrogen balance	1.03

Conversion⁴

% of butane reacted	37.6
% of oxygen reacted	58.2

1. Unsats assumed to be ethylene
2. Other ketones assumed to be diethyl ketone
3. C₃ and higher alcohols assumed to be propanol
4. Conversions based on feed and unreacted component out
5. Oxygen balance and % of reacted oxygen do not include any oxygen in product as H₂O.

TABLE 7
The Effect of 0.906 Second Residence Time

RUN NUMBER B-4		0.372 lb. moles/hr. 0.0159 lb. moles/hr.		125 p.s.i.a. 18.23 ft.	
Feed Rate	Nitrogen-oxygen Butane			Reaction Temperature 725°F.	
Feed Composition	Nitrogen	91.87	mole %	Residence Time	0.906 Seconds
	Oxygen	4.03	mole %	Reynolds Number	4230
	Butane	4.10	mole %		
Duration of test		55.9	minutes		
Total Feed	Nitrogen	0.332	lb. moles		
	Oxygen	0.0145	lb. moles		
	Butane	0.014778	lb. moles		
Reactor Product ⁵		0.0290 lb. atoms O		0.14778 lb. atoms H	
		= 0.059112 lb. atoms C			
Component	Moles	lb. atoms Carbon	lb. atoms Oxygen	lb. atoms Hydrogen	% of Reacted Carbon % of Reacted Oxygen
Butane ¹	0.01049	0.04196	-	0.1049	-
Unsats ¹	0.00210	0.00420	-	0.00840	-
Carbon monoxide	0.00326	0.003266	0.003262	-	28.0
Carbon dioxide	0.00167	0.001667	0.003334	-	21.7
Oxygen	0.00617	-	0.001233 ⁴	-	11.2
Methylethyl ketone	0.000195	0.000780	0.000195	0.001560	-
Acetone	-	-	-	-	5.2
Other ketones ²	0.000130	0.000650	0.000130	0.00130	-
Ethanol	0.000032	0.000064	0.000032	0.000192	4.3
Methanol	0.000325	0.000325	0.000325	0.001300	0.4
C ₃ and higher ³	0.000660	0.001998	0.000666	0.005238	2.2
alcohols ³	0.000682	0.001364	0.000682	0.002728	13.4
Acetaldehyde	0.000682	0.000682	0.000682	0.001364	9.1
Formaldehyde	0.333	-	-	-	7.3
Nitrogen					4.5
Total		0.014992	0.021642	0.127072	-
					100.0
					100.0

TABLE 7 (Continued)
The Effect of 0.906 Second Residence Time

RUN NUMBER B-4

Material Balances

Carbon balance 0.965
 Oxygen balance 0.747
 Hydrogen balance 0.862
 Nitrogen balance 0.985

Conversion⁴

% of butane converted 29.0
 % of oxygen converted 57.6

1. Unsats assumed to be ethylene
2. Other ketones assumed to be diethyl ketone
3. C₃ and higher alcohols assumed to be propanol
4. Conversions based on feed and unreacted component out
5. Oxygen balance and % of reacted oxygen do not include any oxygen in product as H₂O.

TABLE 8
The Effect of 0.664 Second Residence Time

RUN NUMBER B-5

Feed Rate Nitrogen-oxygen
Butane

Reactor Pressure 125 p.s.i.a.
Reactor Length 13.5 ft.
Reaction temperature 725°F.
Residence Time 0.664 seconds
Reynolds Number 4230

Feed Composition

Nitrogen
Oxygen
Butane

0.372 lb. moles/hr.
0.0161 lb. moles/hr.
91.74 mole %
4.11 mole %
4.15 mole %
36.85 minutes
0.214 lb. moles
0.00978 lb. moles = 0.01956 lb. atoms O
0.009864 lb. moles = 0.039456 lb. atoms C and 0.09864 lb. atoms H

Duration of Test
Total Feed Nitrogen
Oxygen
Butane

Reactor Product⁵

Component	Moles	lb. atoms carbon	lb. atoms oxygen	lb. atoms hydrogen	% of reacted carbon	% of reacted oxygen
Butane ¹	0.00814	0.03256	-	0.0814	-	-
Unsats ¹	0.000347	0.000695	-	0.001388	8.1	-
Carbon monoxide	0.000977	0.000977	0.000977	-	11.3	11.4
Carbon dioxide	0.002676	0.002676	0.005352	-	31.0	62.2
Oxygen	0.008269	-	0.016538	-	-	-
Methylethyl ketone	0.000089	0.000356	0.000089	0.000712	4.1	1.0
Acetone	-	-	-	-	-	-
Other ketones ²	0.000089	0.000445	0.000089	0.000890	5.2	1.0
Ethanol	0.000119	0.000238	0.000119	0.000714	2.8	1.4
Methanol	0.000149	0.000149	0.000149	0.000596	1.7	1.7
C ₃ and higher alcohols ³	0.000522	0.001566	0.000522	0.004176	18.1	6.1
Acetaldehyde	0.000209	0.000418	0.000209	0.000836	4.9	2.4
Formaldehyde	0.000103	0.001103	0.001103	0.002206	12.8	12.8
Nitrogen	0.213	-	-	-	-	-

Total 0.041183

0.025147

0.092918

100.0 100.0

TABLE 8 (Continued)
The Effect of 0.664 Second Residence Time

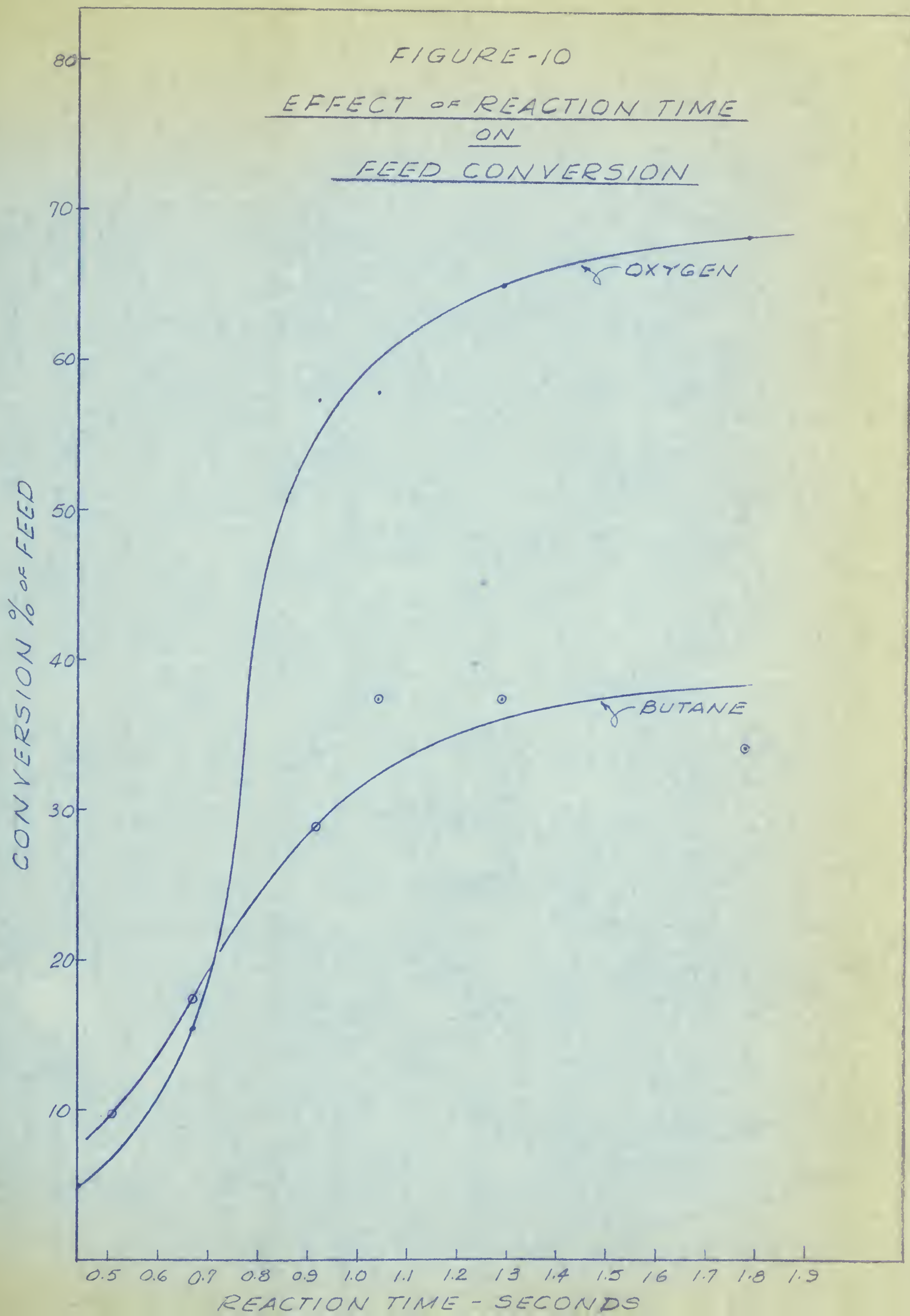
RUN NUMBER B-5

Material Balances

Carbon balance	1.04
Oxygen balance	1.28
Hydrogen balance	0.94
Nitrogen balance	0.995

Conversion ⁴ % of butane converted	17.5
% of oxygen converted	15.5

1. Unsats assumed to be ethylene
2. Other ketones assumed to be diethyl ketone
3. C₃ and higher alcohols assumed to be propanol
4. Conversions based on feed and unreacted component out
5. Oxygen balance and % of reacted oxygen do not include any oxygen in product as H₂O.



PERCENT OF REACTED BUTANE

60

50

40

30

20

10

FIGURE 11

THE EFFECT OF RESIDENCE TIME
ON
BUTANE SELECTIVITY

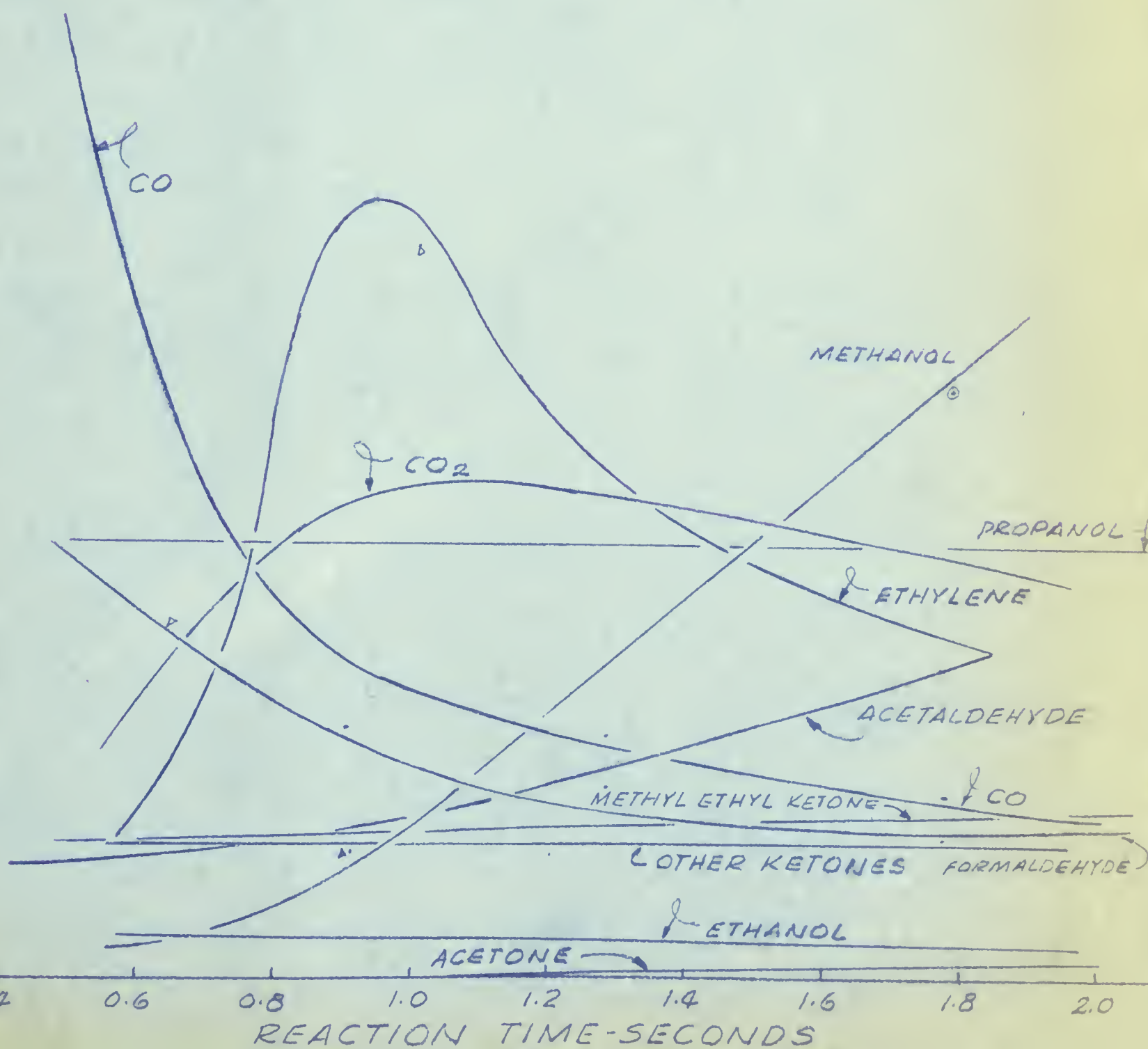
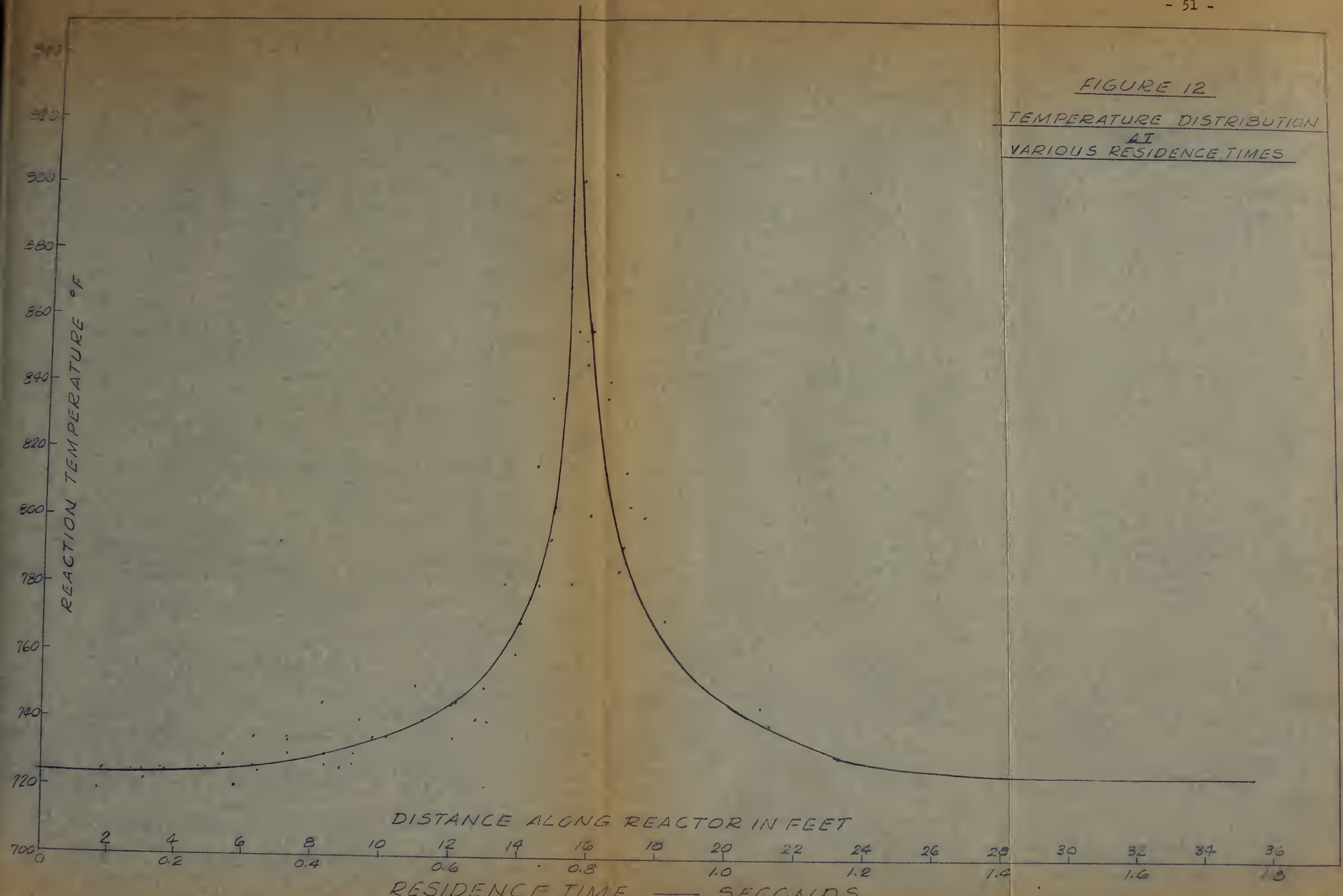


FIGURE 12
TEMPERATURE DISTRIBUTION
AT
VARIOUS RESIDENCE TIMES



place after this time.

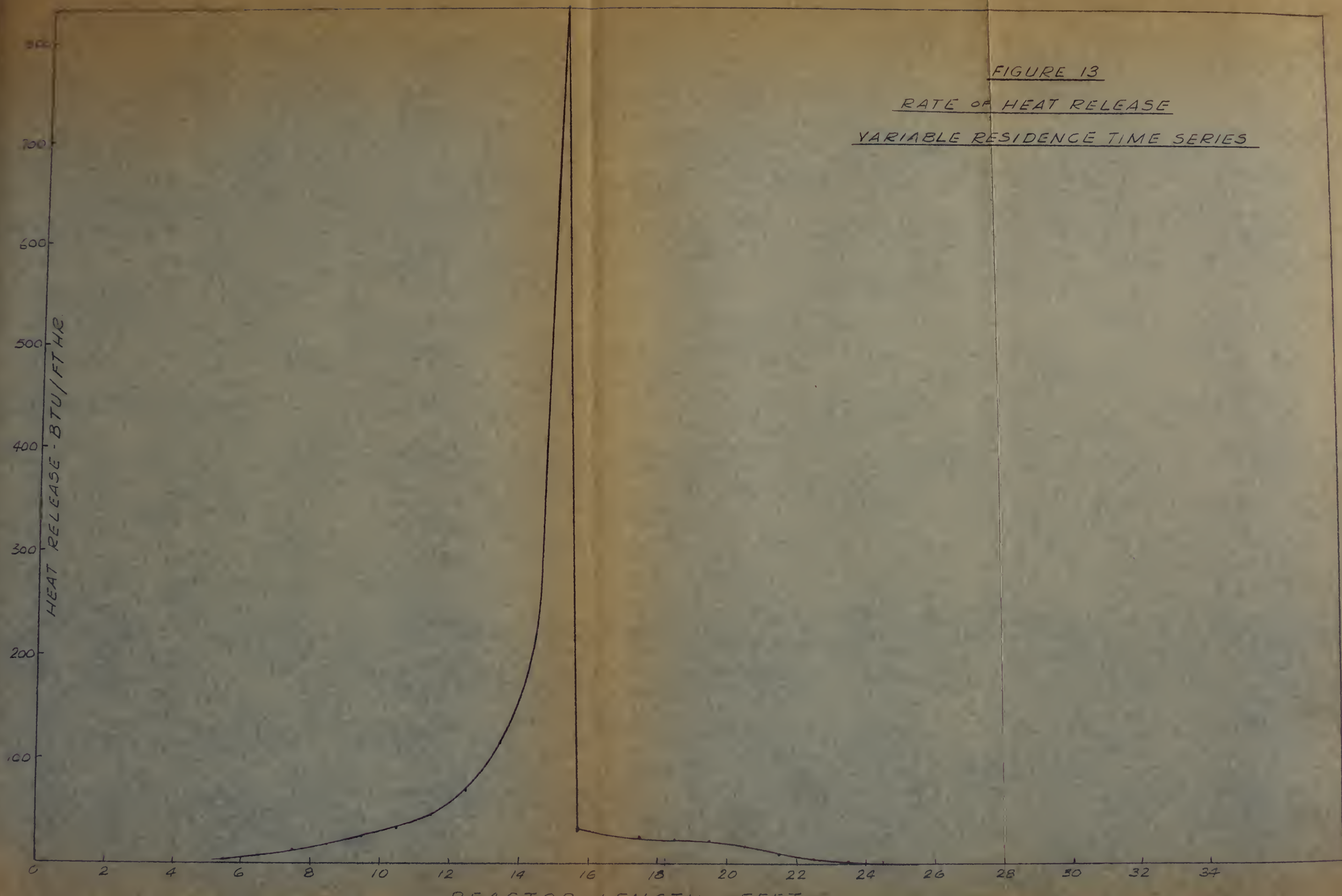
Heat Release

The rate of heat release along the reactor was calculated and is shown as Figure 13. It can be seen that the heat release builds up slowly with a sharp increase in rate as peak reaction rate is approached. Once past the peak reaction rate there is practically no further heat released, indicating that the reaction is essentially complete.

Heats of reaction were calculated from the heats of formation of the reactor feed and products. A comparison of the rate of heat release calculated from the thermal histories and the enthalpy balance based on the reactor feed and product compositions for each of the variable residence time runs is presented as Table 9.

Table 9
Comparison of Heat Release Data

Run	Residence Time Seconds	Rate of Heat Release	
		from temperature profile	from reaction products
B-1	1.77	1140	1050
B-2	1.28	1140	566
B-3	1.03	1090	1130
B-4	0.91	1050	254
B-5	0.66	298	707
B-6	0.53	111	not available



The values calculated from the heat of formation of the reactants and reactor product analysis are very susceptible to errors in the analytical results. This leaves them less reliable than those calculated from the reactor temperature patterns. In view of this, the discrepancies in some of the runs are not surprising.

The reaction pattern is typical of a chain type reaction. At first little reaction takes place but during this time an intermediate compound is formed which acts as a promotor, or chain carrier, for the primary reaction. As the concentration of the chain carrier increases the reaction rate increases exponentially to the point where the reaction rate becomes "explosively fast". The reactants are rapidly consumed and the reaction rate drops off very quickly. The reaction product analysis would indicate that some C_1 or C_2 intermediate is probably the chain carrier as the selectivities to form ethylene, carbon dioxide and carbon monoxide are highest at the low residence times. It is possible that saturated molecules of lower molecular weight were formed but could not be recognized with the analytical methods used.

The Effect of Mass Velocity

The series of runs to examine the effect of mass velocity was run by injecting the feed at different points along the reactor and adjusting the flow rates to give a constant residence time. Runs were made with Reynolds Numbers of 5,340, 4,230, 2,470, and 1,635. All runs were made at 725°F. reaction initiation temperature and 125 p.s.i.a. reaction pressure.

The effect of the mass velocity on the thermal history of the reaction is shown as Figure 14. Reaction feed and product compositions are shown in Tables 10, 11, 12 and 13. It can be seen from the temperature patterns that mass velocity plays an important part in the reaction. The runs with low mass velocities show significantly shorter induction periods and higher temperature surges. The shorter induction periods could be a result of a lower rate of heat transfer from the reaction mixture or a reduced effect of the surface on the reaction under the less turbulent flow conditions. The two runs at high mass velocity exhibit approximately the same induction period indicating a second factor has become the controlling step. This could well be the rate of heat transfer away from the reaction zone.

In the second part, the document provides a detailed overview of the various methods used to collect and analyze data. It describes the different types of data sources, such as surveys, interviews, and focus groups, and explains how this information is used to identify trends and patterns. The document also discusses the challenges associated with data collection and analysis, such as ensuring the reliability and validity of the data.

The third part of the document focuses on the development and implementation of policies and procedures. It outlines the steps involved in creating a comprehensive framework for managing the organization's resources, including the establishment of clear goals and objectives. The document also discusses the importance of regular monitoring and evaluation to ensure that the policies and procedures are effective and up-to-date.

In the final part, the document provides a summary of the key findings and conclusions. It highlights the main points discussed throughout the document and offers recommendations for future research and action. The document concludes by emphasizing the need for continued collaboration and communication among all stakeholders to ensure the success of the project.

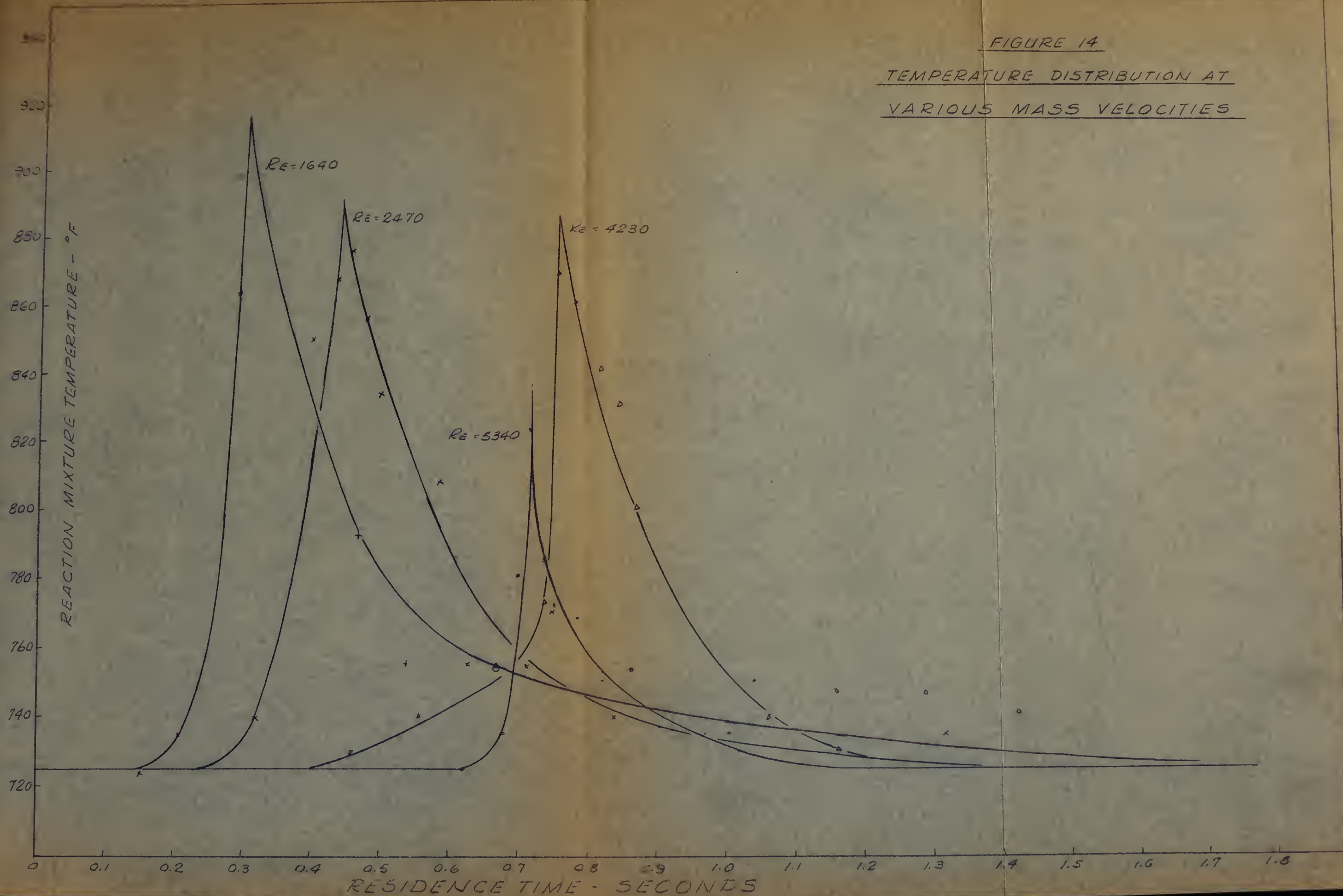


TABLE 10
The Effect of Mass Velocity (Reynolds Number 5340)

RUN NUMBER C-1

Feed Rate	Nitrogen-oxygen Butane	0.470 0.0195	lb. moles/hr. lb. moles/hr.	Reactor Pressure 125 p.s.i.a. Reactor Length 42.64 ft. Reaction temperature 725°F. Residence time 1.68 seconds Reynolds Number 5340
Feed Composition	Nitrogen Oxygen Butane	91.93 4.09 3.98	mole % mole % mole %	
Duration of Test		50.05	minutes	
Total Feed Nitrogen		0.376	lb. moles	
Oxygen		0.0168	lb. moles	0.0336 lb. atoms O
Butane		0.016202	lb. moles	0.064808 lb. atoms C and 0.16202 lb. atoms H

Reactor Product⁵

Component	Moles	lb. atoms carbon	lb. atoms oxygen	lb. atoms hydrogen	% of reacted carbon	% of reacted oxygen
Butane ₁	0.01245	0.04980	-	0.1245	-	-
Unsats ₁	0.00164	0.00328	-	0.00656	22.6	-
Carbon monoxide	0.003323	0.003323	0.003323	-	22.9	29.3
Carbon dioxide	0.002783	0.002783	0.005566	-	19.2	49.2
Oxygen	0.005274	-	0.010548	-	-	-
Methylethyl ketone	0.000192	0.000768	0.000192	0.001536	5.3	1.7
Acetone	0.000085	0.000255	0.000085	0.000510	1.8	0.8
Other ketones ²	0.000107	0.000535	0.000107	0.001070	3.7	0.9
Ethanol	0.000064	0.000128	0.000064	0.000384	0.9	0.6
Methanol	0.000299	0.000299	0.000299	0.001196	2.1	2.5
C ₃ and higher ³						
alcohols	0.000470	0.001410	0.000470	0.003760	9.7	4.1
Acetaldehyde	0.000470	0.000940	0.000470	0.001880	6.5	4.1
Formaldehyde	0.000796	0.000769	0.000769	0.001538	5.3	6.8
Nitrogen	0.364	-	-	-	-	-
Total		0.06429	0.021893	0.14293	100.0	100.0

TABLE 10 (Continued)
The Effect of Mass Velocity (Reynolds Number 5340)

RUN NUMBER C-1

Material Balances

Carbon balance 0.99
 Oxygen balance 0.652
 Hydrogen balance 0.881
 Nitrogen balance 0.969

Conversion⁴

% of butane converted 23.1
 % of oxygen converted 68.4

1. Unsats assumed to be ethylene
2. Other ketones assumed to be diethyl ketone
3. C₃ and higher alcohols assumed to be propanol
4. Conversions based on feed and unreacted component out
5. Oxygen balance and % of reacted oxygen do not include any oxygen in product as H₂O.

TABLE 11
The Effect of Mass Velocity (Reynolds Number 4230)

RUN NUMBER C-2 (As A-3)

Feed Rate	Nitrogen-oxygen	0.372	lb. moles/hr.	Reactor Pressure	125 p.s.i.a.
	Butane	0.0162	lb. moles/hr.	Reactor length	38.58 ft.
Feed Composition				Reaction temperature	725°F.
	Nitrogen	91.81	mole %	Residence time	1.77 seconds
	Oxygen	4.02	mole %	Reynolds Number	4230
	Butane	4.17	mole %		
Duration of Test		53.1	minutes		
Total Feed Nitrogen		0.308	lb. moles		
	Oxygen	0.01345	lb. moles	0.02690 lb. atoms O	
	Butane	0.01397	lb. moles	0.05588 lb. atoms C and 0.1397 lb. atoms H	

Reactor Product⁵

Component	Moles	lb. atoms carbon	lb. atoms oxygen	lb. atoms hydrogen	% of reacted carbon	% of reacted oxygen
Butane ¹	0.00912	0.03648	-	0.0912	-	-
Unsats	0.00137	0.00274	-	0.00548	11.2	-
Carbon monoxide	0.00366	0.00366	0.00366	-	15.0	21.5
Carbon dioxide	0.00155	0.00155	0.00310	-	6.3	18.1
Oxygen	0.00421	-	0.00842	-	-	-
Methylethyl ketone	0.000394	0.001576	0.000394	0.003153	6.4	2.3
Acetone	0.000036	0.000108	0.000036	0.000216	0.4	0.2
Other ketones ²	0.000251	0.001255	0.000251	0.002510	5.1	1.5
Ethanol	0.000107	0.000214	0.000107	0.000642	0.9	0.6
Methanol	0.005214	0.005214	0.005214	0.020856	21.3	30.8
C ₃ and higher ³						
alcohols	0.001254	0.003762	0.001254	0.012032	15.4	7.3
Acetaldehyde	0.001397	0.002794	0.001397	0.005588	11.3	8.2
Formaldehyde	0.001648	0.001648	0.001648	0.003926	6.7	9.7
Nitrogen	0.3065	-	-	-	-	-
Total		0.061003	0.02549	0.14497	100.0	100.0

TABLE 11 (Continued)
The Effect of Mass Velocity (Reynolds Number 4230)

RUN NUMBER C-2 (As A-3)

Material balances

Carbon balance	1.09
Oxygen balance	0.947
Hydrogen balance	1.04
Nitrogen balance	0.996

Conversion⁴

% of butane reacted	34.7
% of oxygen reacted	68.6

1. Unsats assumed to be ethylene
2. Other ketones assumed to be diethyl ketone
3. C₃ and higher alcohols assumed to be propanol
4. Conversions based on feed and unreacted component out
5. Oxygen balance and % of reacted oxygen do not include any oxygen in product as H₂O.

TABLE 12
The Effect of Mass Velocity (Reynolds Number 2470)

RUN NUMBER C-3

Feed Rate	Nitrogen-oxygen Butane	0.219 0.00806	lb. moles/hr. lb. moles/hr.	Reactor pressure 125 p.s.i.a. Reactor length 20.79 ft. Reaction temperature 725°F. Residence time 1.76 seconds Reynolds number 2470
Feed Composition	Nitrogen Oxygen Butane	92.4 4.0 3.6	mole % mole % mole %	
Duration of Test		52.15	minutes	
Total Feed	Nitrogen Oxygen Butane	0.182 0.00789 0.007006	lb. moles lb. moles lb. moles	

= 0.01578 lb. atoms C
= 0.028024 lb. atoms H

Reactor Product⁵

Component	Moles	lb. atoms carbon	lb. atoms oxygen	lb. atoms hydrogen	% of reacted carbon	% of reacted oxygen
Butane ¹	0.00510	0.02040	-	0.05100	-	-
Unsats	0.00101	0.00202	-	0.00404	12.1	-
Carbon monoxide	0.003198	0.003198	0.003198	-	18.9	22.7
Carbon dioxide	0.002249	0.002249	0.004498	-	13.1	32.0
Oxygen	0.002199	-	0.004398	-	-	-
Methylethyl ketone	0.000036	0.000144	0.000036	0.000288	0.8	0.3
Acetone	0.000036	0.000108	0.000036	0.000216	0.6	0.3
Other ketones ²	0.000145	0.000725	0.000145	0.001450	4.3	1.0
Ethanol	0.000072	0.000144	0.000072	0.000432	0.8	0.5
Methanol	0.001228	0.001228	0.001228	0.004912	7.2	8.7
C ₃ and higher alcohols ³	0.000849	0.002547	0.000849	0.006792	15.2	6.0
Acetaldehyde	0.000542	0.001084	0.000542	0.002168	4.6	3.8
Formaldehyde	0.003468	0.003468	0.003468	0.006936	20.6	24.7
Nitrogen	0.190	-	-	-	-	-
Total		0.037315	0.01847	0.07833	100.0	100.0

TABLE 12 (Continued)
The Effect of Mass Velocity (Reynolds Number 2470)

RUN NUMBER C-3

Material Balances

Carbon balance	1.33
Oxygen balance	1.17
Hydrogen balance	1.12
Nitrogen balance	1.04

Conversion⁴

% of butane converted	27.3
% of oxygen converted	72.1

1. Unsats assumed to be ethylene
2. Other ketones assumed to be diethyl ketone
3. C₃ and higher alcohols assumed to be propanol
4. Conversions based on feed and unreacted component out
5. Oxygen balance and % of reacted oxygen do not include any oxygen in product as H₂O.

TABLE 13
Effect of Mass Velocity (Reynolds Number 1635)

RUN NUMBER C-4

Feed Rate	Nitrogen-oxygen Butane	0.144 0.00591	lb. moles/hr. lb. moles/hr.	Reactor pressure Reactor length Reaction temperature Residence time Reynolds Number	125 p.s.i.a. 13.51 ft. 725°F. 1.72 seconds 1635
Feed Composition	Nitrogen Oxygen Butane	mole % mole % mole %			
Duration of Test		minutes			
Total Feed Nitrogen		lb. moles			
Oxygen		lb. moles		0.01008 lb. atoms O	
Butane		lb. moles		0.019224 lb. atoms C and 0.04806 lb. atoms H	

Reactor Product⁵

Component	Moles	lb. atoms carbon	lb. atoms oxygen	lb. atoms hydrogen	% of reacted carbon	% of reacted oxygen
Butane ¹	0.00258	0.01032	-	0.02580	-	-
Unsats ¹	0.00079	0.00158	-	0.00316	13.9	-
Carbon monoxide	0.002916	0.002916	0.002916	-	25.8	33.5
Carbon dioxide	0.001802	0.001802	0.003604	-	15.9	41.3
Oxygen	0.001322	-	0.002644	-	-	-
Methylethyl ketone	0.000213	0.000852	0.000213	0.001704	7.5	2.5
Acetone	-	-	-	-	-	-
Other ketones ²	0.000107	0.000535	0.000107	0.001070	4.7	1.2
Ethanol	0.000043	0.000086	0.000043	0.000258	0.8	0.5
Methanol	0.000213	0.000213	0.000213	0.000852	1.9	2.5
C ₃ and higher alcohols ³	0.000789	0.002367	0.000789	0.006312	20.9	9.1
Acetaldehyde	0.000171	0.000342	0.000171	0.000684	3.0	2.0
Formaldehyde	0.000640	0.000640	0.000640	0.001280	5.6	7.4
Nitrogen	0.110	-	-	-	-	-
Total		0.021653	0.01134	0.041120	100.0	100.0

TABLE 13 (Continued)
Effect of Mass Velocity (Reynolds Number 1635)

RUN NUMBER C-4

Material Balances

Carbon balance	1.13
Oxygen balance	1.07
Hydrogen balance	0.857
Nitrogen balance	0.984

Conversion⁴

% of butane converted	46.4
% of oxygen converted	71.6

1. Unsats assumed to be ethylene
2. Other ketones assumed to be diethyl ketone
3. C₃ and higher alcohols assumed to be propanol
4. Conversions based on feed and unreacted component out
5. Oxygen balance and % of reacted oxygen do not include any oxygen in product as H₂O.

The effect of mass velocity on feed conversion is shown in Figure 15. Figure 16 shows the selectivity to form the various compounds found in the reactor product at the different mass velocities.

DISCUSSION OF RESULTS

Temperature Measurements

The temperature measurements taken during the experimental program provided a very good measure of the reaction characteristics. In all runs the reaction could be broken down into an "induction period", where the reaction rate began to build up, an "explosive type reaction" with a rapidly increasing reaction rate and a "cooling off period" where little reaction is taking place. These measurements offered an immediate method of measuring the reaction and provided a qualitative history of the reaction taking place.

Reaction Product

The reaction product data shows the compounds formed at the different reaction conditions. The data indicated poor component balances in some of the runs so that in each case the product results were examined as

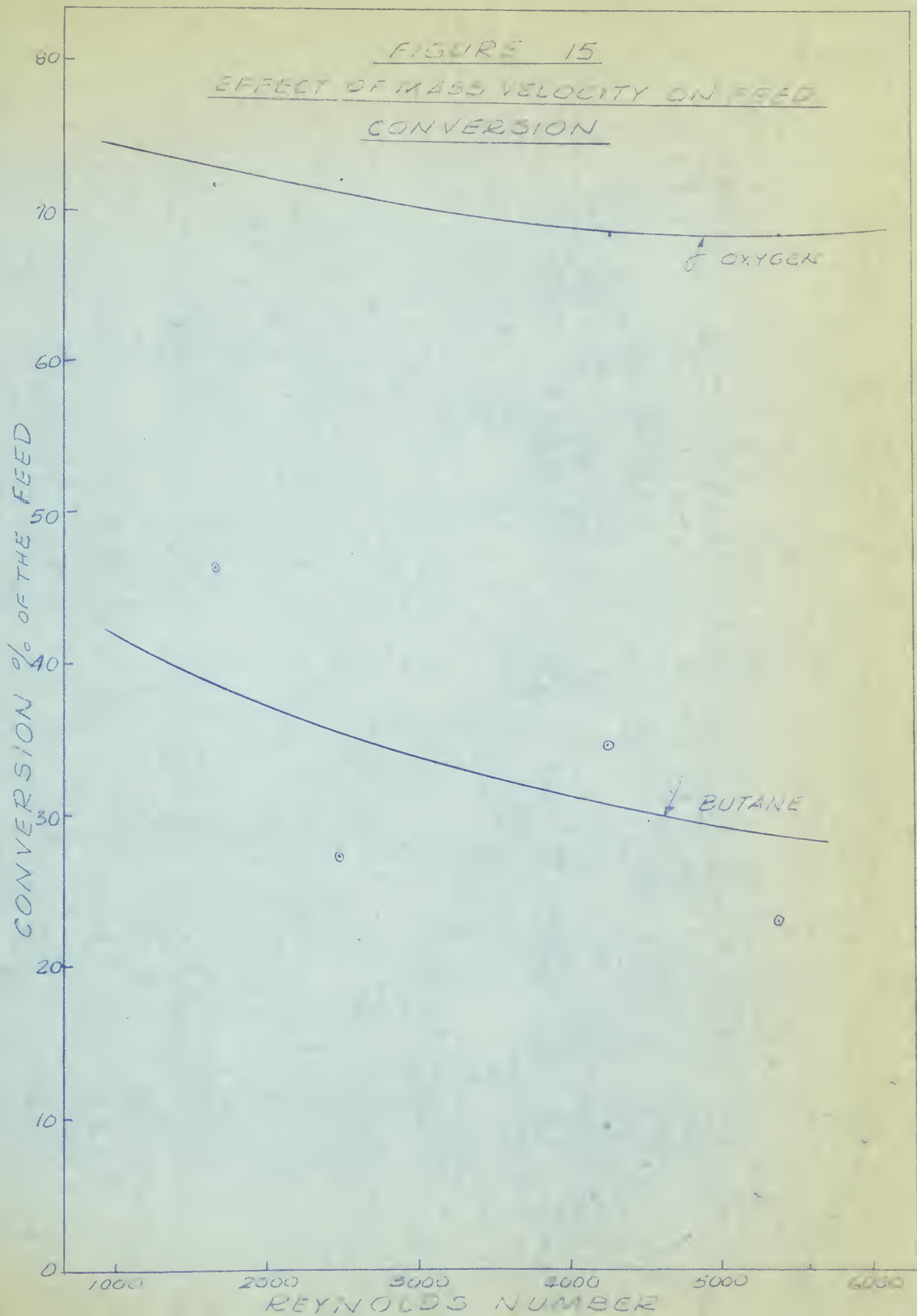
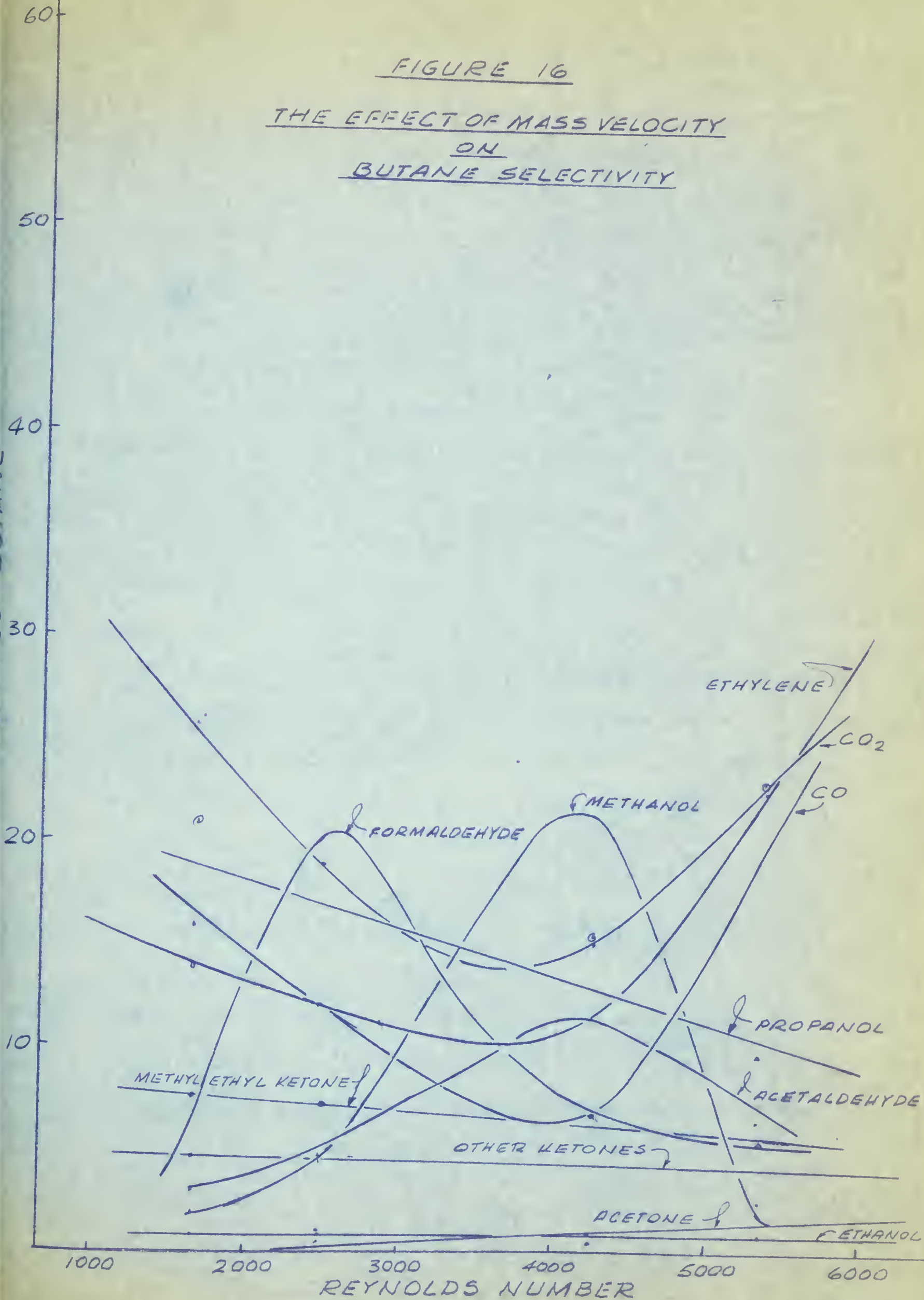


FIGURE 16

THE EFFECT OF MASS VELOCITY
ON
BUTANE SELECTIVITY

PERCENT BUTANE



a portion of the reacted feed. The reacted oxygen based on the continuous analyses is the best measure of the reaction. Reacted butane is probably second best but this is based on orsat analyses which are not quite so reliable. The liquid product data cannot be considered very accurate since dilute water samples are very difficult to analyze. Possible sample contamination further complicates the liquid product analysis. However, these data do provide an indication of the reaction trends.

During the Reaction Initiation Temperature Tests methanol appears to be the chief product at the lower temperatures. Methanol gives away to carbon monoxide, carbon dioxide and ethylene at the higher temperatures. All other compounds except acetone remained fairly constant, in their relative formation rates, during the series of tests. Acetone was only formed during the low temperature (low conversion) runs.

During the series at various residence times the product distribution based on the butane converted shows a large amount of butane forming carbon monoxide during the low conversion runs. As the conversion increases ethylene is favoured going through a peak production at about 0.9 seconds residence time (near

period of maximum temperature) with lesser amounts formed at the higher residence time. Other compounds except acetone are formed at nearly constant proportions at the different residence times. Acetone was only formed at the higher residence times.

The tests at various Mass Velocities shows the formation of formaldehyde, acetaldehyde and methanol increase to maximums and then drop off as the mass velocity is increased. Carbon monoxide, carbon dioxide and ethylene show a decrease through a minimum and then increase as the mass velocity is increased. Acetone was not formed during the run at the lowest mass velocity.

CONCLUSIONS

The Reactor

The reactor design used for this study was adequate for the proposed test program. The variable effective length of the reactor made it possible to stop the reaction at a variety of reaction times. The thermocouple arrangement provided a means to obtain a continuous measure of the reaction temperature through the reaction zone as was planned in the reactor design.

The reactor bath, on the other hand, was far from satisfactory. Continual use of Aroclor at its boiling point causes the compound to break down. This decomposition was accelerated when the boiling point of aroclor was increased by increasing the pressure on the reactor bath. In the final phase of the test work, when an attempt was made to operate at 775°F., the decomposition became so rapid that a pressure build-up occurred in the vessel. The decomposition compounds had fouled the pressure release and the bypass to the point where they were inoperable. The pressure, well in excess of the range of the 60 p.s.i. gauge attached to the condenser, could have resulted in a rupture of the bath, since

it had been subjected to severe corrosion by hydrochloric acid, one of the decomposition compounds.

It is highly recommended that a new type of temperature bath be designed before too much further work is done on this project.

Other possible baths include a variety of salts or metals which can be held at their melting point or maintained as a liquid. Baths of this type are undesirable, however, because of the corrosion problems associated with salts and the toxic fumes from metals. Metals also present handling problems making them undesirable.

A suitable bath for the study of hydrocarbon oxidation reactions could be constructed using a fluidized particle bed. The design of a constant temperature bath for use in pilot plant studies is described by Adams (1). The bath uses a bed of graded fine solids such as sand, fluid cracking catalyst or any other suitable material, fluidized by a hot air stream. Heat can be applied to the system by external heaters, preheated air or by injecting fuel directly into the fluidized bed. Such a reactor bath would be capable of operating over a much wider range of temperatures and would be much less hazardous than the Aroclor baths used for present work or either a molten salt or metal.

Summary of Results

The series of tests to study the effect of residence time indicate clearly the effect of time on the reaction. There is an induction period, where only limited reaction takes place, a period of increasing reaction rate, where the reactants are consumed, and a period of little or no reaction lasting for the remainder of the residence time. This general pattern was followed in all tests where the residence time was long enough and the temperature high enough to permit the reaction to take place.

The relative times for each of these "phases" of the reaction did change, however, as the other variables were changed. Certainly the change in induction period with a change in reaction initiation temperature was a thermal effect. The change of induction period with a change in mass velocity, could be a thermal effect, brought about by a decrease in the heat transfer from the reaction, or it could be the result of a change in the influence of the reactor surface under the less turbulent flow conditions. The effect of surface then is one variable that should be examined further.

The effect of surface could be examined by adding surface in the reactor in the form of packing. The packing material must be one that will remain completely non-catalytic for the reaction studied. Metals may not be acceptable as their oxides can serve as oxidation catalysts. Ceramic packings are probably more desirable.

If the change in the reaction characteristics with change in mass velocity is purely thermal, it should be possible to measure the effect separately by changing the feed composition or by changing the heat transfer independent of the reaction mixture. The reaction diluent serves two purposes; it reduces the partial pressure of the reactants and serves as a heat sink for the heat of reaction. A thermal effect should then be measurable by a change in feed composition along with the appropriate change in pressure to hold the partial pressure of the reactants constant. A diluent gas of different heat capacity would also provide a method of measuring the thermal effect on the reaction.

A reactor bath of the type described above may provide a method of measuring the thermal effects. If the heat transfer from the outer surface of the reactor could be reduced to where it plays a significant

part in the overall heat transfer coefficient, the thermal effects on the reaction rate could be studied without changing the reaction flow rates. The rate of heat transfer could possibly be varied by changes in the fluidization air flow rates or by changing the fluidized particles, using a particle of different heat capacity.

FUTURE TESTS

The reaction variables studied in the series of tests conducted to date, to study the hydrocarbon oxidation reaction, have been very limited in range and have only been varied one at a time. These studies, then, show only the effect of one variable while all others are constant. As a result any interactions between variables is undetected. There is no doubt, however, that interactions do exist. There are indications of some interaction between reaction initiation temperature and mass velocity.

It is probable that the reaction will take place at conditions eliminated before if more than one variable is varied at a time.

It is proposed that future tests take the form of a "Factorial Experiment", as described by Davies (6), where all the variables are studied at all levels of

the other variables under investigation. The data from such a test can be studied mathematically to determine the effect of each variable on the reaction.

The variables to be included in such a study would include; oxygen-butane ratio, diluent gas concentration, reactor pressure, reactor temperature, mass velocity, surface area, heat transfer rate, diluent gas, and any others that may influence the reaction. Each of the variables should be studied at three, or preferably four levels. This would result in a fairly long experimental program. The length of the program would not be as much of a problem as it was before the development of gas chromatography for gas analysis. The analytical work could be done between runs allowing a repetition of runs that appeared doubtful.

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APPENDIX

Nomenclature

A	-	area, ft. ²
C _p	-	heat capacity, B.T.U./lb./°F.
D	-	diameter, ft.
D _e	-	equivalent diameter, ft.
G	-	mass rate of flow, lb.ft. ² /hr.
h	-	film heat transfer coefficient, B.T.U./ft. ² hr.°F.
k	-	thermal conductivity, B.T.U./ft. ² hr.°F./ft.
l	-	length, ft.
M	-	molecular weight, lb.
p	-	perimeter, ft.
Q	-	heat release, B.T.U.
R	-	gas constant cu. ft. - lb./in. ² /°R/mole.
Re	-	Reynolds Number
T	-	temperature of gas, °F.
T _b	-	temperature of the bath, °F.
dt	-	temperature rise, °F.
ΔT _{lm}	-	log mean temperature difference, °F.
U	-	overall heat transfer coefficient, B.T.U./ft. ² hr.°F.
V	-	velocity, ft./sec.
w	-	flow rate, lb./hr.
μ	-	viscosity, lb./ft./hr.

Reactor Design

The previous work on the partial oxidation of butane indicated interesting thermal effects were present during the reaction. However, the reactor used for those studies was of a fixed length with only five temperature measuring points along its entire length. A new reactor was to be designed for the present studies that would allow a more complete thermal history of the reaction. It was also required that the effective length of the reactor be variable. The final design of the reactor, using interconnected U shaped pipes with axial thermowells, has been discussed earlier. The sizing of the reactor required that the reactor be of a reasonable length and that it would require flow rates practicable in the laboratory. The design was to provide a 2 second residence time under fully developed turbulent flow. Wiegand (19) indicates that turbulence is fully developed in an annular space with a Reynolds Number slightly greater than 2000. In order to conduct a variety of tests with turbulent flow a design Reynolds number of 4000 was used.

Design Conditions

Residence time, seconds 2.0

Flowing temperature, °F., 725

Flowing pressure, p.s.i.a. 125

Reynolds Number, 4000

It was found that if a nominal $\frac{1}{4}$ inch stainless steel pipe was used with a $3/16$ inch o.d. thermowell the design conditions could be met.

$$Re = \frac{De G}{\mu}$$

$$Re = 4000$$

$$\begin{aligned} De &= (0.0303 - 0.0156) \text{ ft.} \\ &= 0.0147 \text{ ft.} \end{aligned}$$

$$\mu = 0.075 \text{ lb./ft./hr.}$$

$$\begin{aligned} G &= \frac{(4000)(0.075)}{(0.0147)} \\ &= 20,400 \text{ lb./ft.}^2/\text{hr.} \end{aligned}$$

$$G = w/A$$

$$A = 0.00053 \text{ ft.}^2$$

$$\begin{aligned} w &= (20,400)(0.00053) \\ &= 10.8 \text{ lb./hr.} \end{aligned}$$

Velocity in the annulus

$$\begin{aligned}
 V &= \frac{w R T}{P M A (3600)} \quad \text{ft./sec.} \\
 &= \frac{(10.8)(10.73)(1185)}{(125)(29)(0.00053)(3600)} \\
 &= 19.9 \text{ ft./sec.}
 \end{aligned}$$

Length of reactor required for 2 seconds residence time is 39.8 ft.

The gas flow rate (10.8 lb./hr.) and the reactor length (39.8 ft.) were considered to be reasonable.

Nitrogen-Oxygen Preheater.

The nitrogen-oxygen stream was to be preheated to approximately the reactor temperature before entering the reactor. The preheating would take place in a $\frac{1}{4}$ inch o.d. stainless steel tube immersed in the reactor bath. A heat balance on the preheat tube established the approximate length of preheater required.

$$UA\Delta T_{lm} = wC_p dt$$

Dalla Lana's work indicates the outside film coefficient of the Aroclar bath is 25 B.T.U./ft.² hr.⁰F., based on the outside area. Based on the inside surface of the tube this becomes $\frac{(0.25)}{(0.18)} (25) = 35 \text{ B.T.U./ft.}^2 \text{ hr.}^0 \text{F.}$ (The inside diameter of the tube was 0.180 in.)

The gas film coefficient on the inside of the tube was calculated by the Dittus-Boelter equation.

$$\frac{hD}{k} = 0.023 \left(\frac{C_p \mu}{k} \right)^{0.4} \left(\frac{DG}{\mu} \right)^{0.8}$$

where $D = 0.015$ ft.

$$k = 0.024 \text{ B.T.U./ft.}^2\text{hr.}^\circ\text{F./ft.}$$

$$G = 61,200 \text{ lb./ft.}^2\text{hr.}$$

$$\mu_{av} = 0.060 \text{ lb./ft.hr.}$$

$$C_p = 0.26 \text{ B.T.U./lb.}^\circ\text{F.}$$

$$h = \frac{(0.024)}{(0.015)} (0.023) \frac{(26)(0.060)}{(0.024)} \frac{(0.015)(61,200)}{(0.060)}$$

$$= 75.0 \text{ B.T.U./ft.}^2\text{hr.}^\circ\text{F.}$$

The overall heat transfer coefficient U was calculated by:

$$\frac{1}{U} = \frac{1}{35} + \frac{1}{75}$$

$$U = 22.2 \text{ B.T.U./hr.ft.}^2 \text{ }^\circ\text{F.}$$

$$wC_p dt = UA\Delta T_{lm}$$

$$w = 10.8 \text{ lb./hr.}$$

$$C_p = 0.26 \text{ B.T.U./lb.}^\circ\text{F.}$$

$$dt = (725 - 70) = 655^\circ\text{F.}$$

$$A = 0.0471 \text{ ft.}^2/\text{ft. of length}$$

$$\Delta T_{lm} = \frac{(725 - 70) - (725 - T_2)}{\ln \frac{(725 - 70)}{(725 - T_2)}}$$

The heat balance equation was solved by trial and error, by assuming a preheater length and calculating the outlet temperature. A preheater length of 16 feet gave a calculated outlet temperature of 723°F. This was considered adequate.

Butane Preheater

The butane feed was vapourized and partially preheated in a separate boiling bath of Aroclor. The hot butane vapour was transferred from the bath to the reactor inlet in an electrically heated line. Final preheating took place in the axial feed line in the reactor. The temperature of the butane entering the reactor could be adjusted by adjusting the temperature of the Aroclor bath or by adjusting the electrical power to the electrical heater on the inlet line.

Reaction Quenching

In order to stop the reaction immediately after the gases left the reactor a double pipe heat exchanger was constructed and placed on the reactor outlet.

Exchanger Design

The exchanger was designed to quench the reaction products to well below the reaction initiation temperature. The exchanger was constructed from an eighteen inch length of $\frac{1}{4}$ inch pipe with coaxial $\frac{1}{4}$ inch o.d. water tube. Heat transfer coefficients were calculated using the Dittus-Boelter equation.

$$\frac{hD}{k} = 0.023 (Re)^{0.8} \left(\frac{c_p \mu}{k} \right)^{0.4}$$

for the water side and the modified equation

$$\frac{hD}{k} = 0.038 (Re)^{0.8} \left(\frac{c_p \mu}{k} \right)^{0.33} \left(\frac{D_2}{D_1} \right)^{0.15}$$

for the gas film coefficient on the outer surface of the water tube. The exit temperature of the gas could then be calculated by equating heat balances on the gas stream, the water stream and the overall heat transfer equation.

$$\text{i.e.} \quad Q = w C_{p \text{ gas}} dt_{\text{gas}} = w C_{p \text{ H}_2\text{O}} dt_{\text{H}_2\text{O}} = UA \Delta T_{lm}$$

Heat losses from the outer surface of the pipe were not included in the calculations. The exit temperature of the gas was found to be about 120°F., well below the temperature necessary for reaction.

Back Pressure Control

The back pressure control valve used in the previous studies would not hold the reactor pressure very constant. Inquiries were made to various suppliers for a more accurate valve but none would guarantee their products to give the control requested (125 p.s.i.a. $\pm$ 1 p.s.i.). It had been noted, however, that the "Grove" pressure reducer used on the nitrogen-oxygen supply, was capable of controlling the down stream pressure very accurately over a wide range of flow rates and up stream pressures. It was decided to machine new parts for a "Grove" pressure regulator to use the same principle to control the back pressure. The modified valve showed very good pressure control over the range of flow rates to be used in the studies. Figures A-1 and A-2 show the action of the original and modified valves respectively.

Experimental Runs

During each of the experimental runs where there was evidence of a reaction taking place, a controlled run was made. During the run feed and product flow rates were recorded to allow

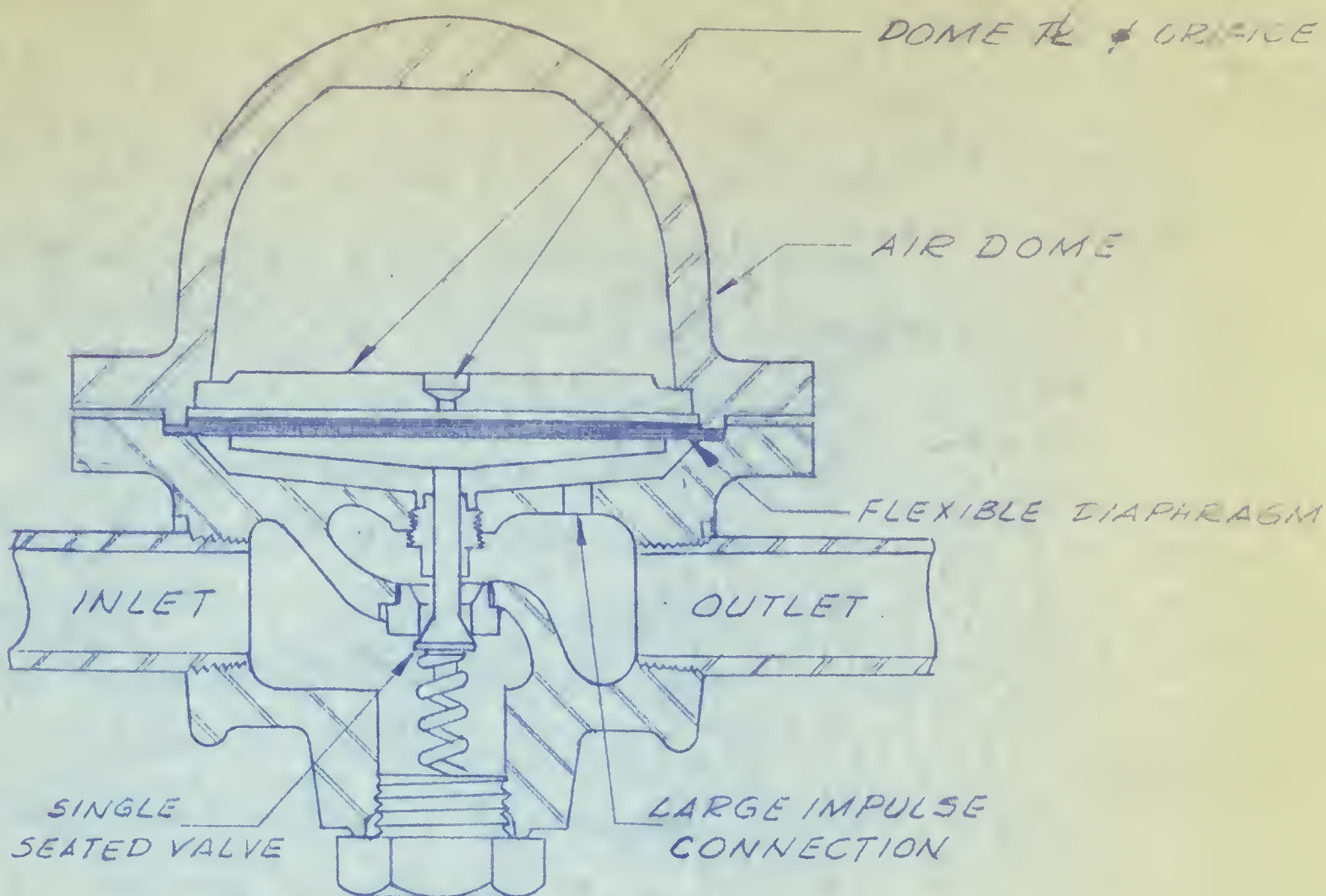


FIGURE A-1 (ORIGINAL VA.)
GROVE PRESSURE REDUCER

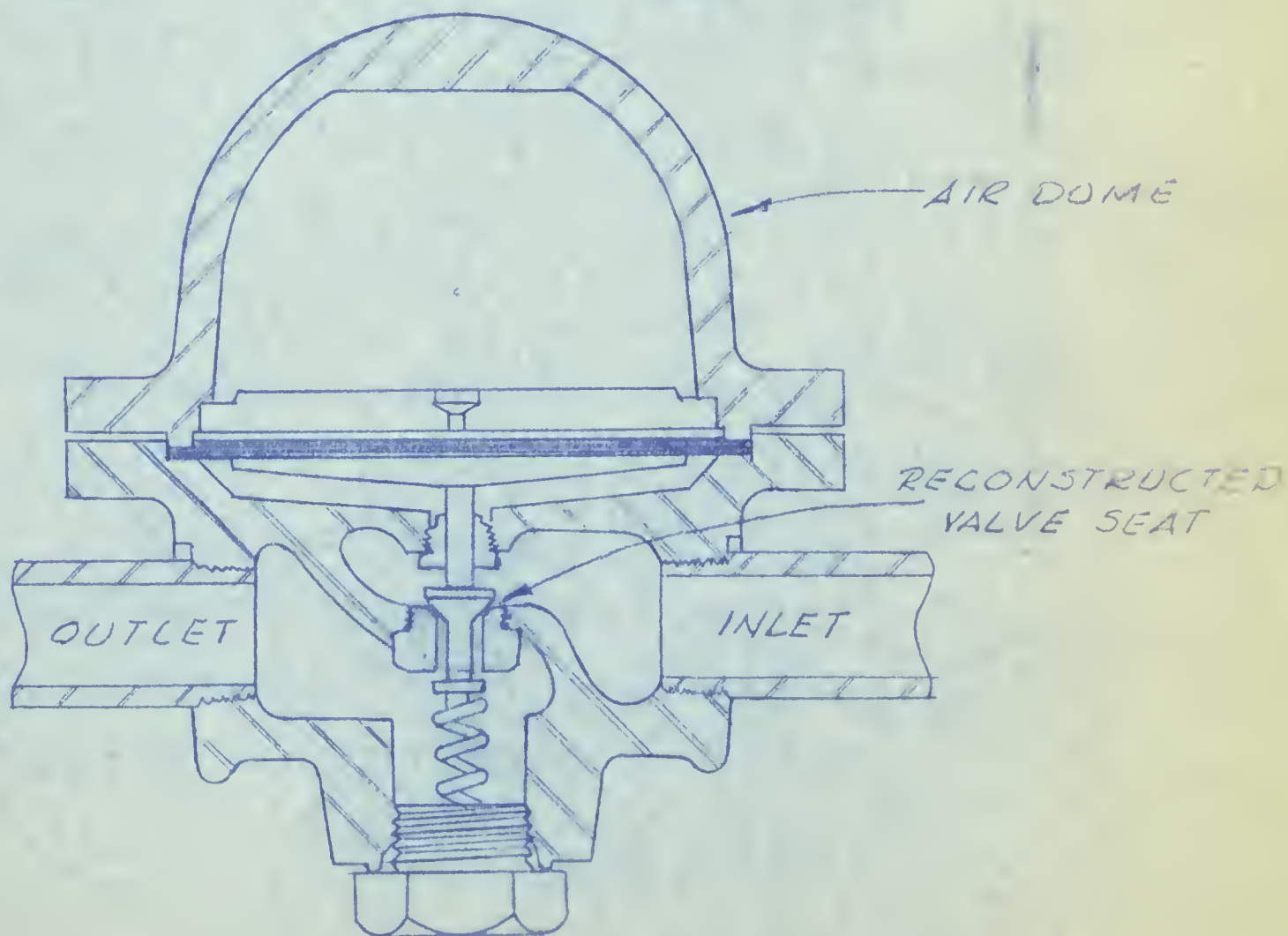


FIGURE A-2 (RECONSTRUCTED VA.)
BACK PRESSURE REGULATOR

material balances on the run. These data are presented as Table A-1. Spot samples of the unabsorbed gases were taken for orsat analysis. The gas analyses are presented as Table A-2. All of the liquid in the absorption column was collected and a sample sent to "Consolidated Engineering Inc." for mass spectrometer analyses. These data are presented as Table A-3. The water in these samples is assumed to be entirely from the absorption column, therefore, none was included in the material balances around the reactor. The carbonyl precipitate in the 2,4- dinitrophenyl hydrazine was non-existent during most of the runs and so small in the others that it was neglected in the work-ups.

Reactor Product Work-up

The gas and liquid product samples were worked up to obtain the amount of each component present. These could then be added together to give the composite reactor product analysis presented in the body of this report. Examples of the work-ups are shown in Tables A-4 and A-5.

TABLE A-1

Experimental Data

Run	A-2	A-3	A-4	B-2	B-3	B-4	B-5	C-1	C-3	C-4
Measurement										
Length of run, minutes	29.64	51.84	63.92	57.62	33.67	55.9	36.85	50.05	52.15	48.90
Atmospheric pressure inches, Hg.	27.7	27.8	27.8	27.8	27.9	27.7	27.7	27.5	27.8	27.7
Outlet gas, ft. ³ pressure, inches Hg. temperature, °C.	Not Taken	134.75 atm. 19.25	166.50 atm. 23.25	143.0 atm. 21.25	81.20 30.0 18.0	145.0 atm. 19.25	96.75 atm. 22.0	161.5 atm. 17.0	83.55 atm. 21.25	48.85 atm. 23.0
Liquid Sample, gm.	1100	1574	1350	1289	1509	1377	1278	912	1549	1799
Phenylhydrazine 3 Gas volume, ft. ³ Temp., °F.	Not Taken	0.3898 72	0.2604 81	0.5388 76	0.065 72	0.2999 72	0.2671 78.5	0.5595 72.0	0.1750 75	0.02562 78
Butane used, c.c. Temperature, °F.	320 Not Taken	619 71	724 84.2	668 76.2	365 64.4	657 74.3	440 78.8	706 61.7	312 76.5	214 77.9

TABLE A-2

Off Gas Analysis Mole Percent

Run	A-2	A-3	A-4	B-2	B-3	B-4	B-5	C-1	C-3	C-4
Component										
Carbon Dioxide	0.1	0.4	0.6	0.48	0.23	0.3	0.1	0.62	0.74	0.56
Carbon Monoxide	0.0	0.84	0.9	0.64	0.68	0.7	0.1	0.72	0.98	1.04
Unsats.	0.4	0.42	0.6	0.46	0.45	0.6	0.15	0.42	0.5	0.68
Butane	2.8	2.8	2.68	2.73	2.39	3.0	3.52	3.2	2.54	2.22
Oxygen	3.5	1.25	0.9	1.50	1.55	1.7	3.5	1.30	0.95	0.70
Nitrogen	93.2	94.29	94.32	94.91	94.70	93.7	92.63	93.74	94.29	94.80
Total	100.00	100.00	100.00	100.00	100.00	100.0	100.00	100.00	100.00	100.00

-A-12-

TABLE A-3

Liquid Product Analysis Mole Percent

[illegible]

TABLE A-4

Off Gas Work-up for Run A-3

Total flow 134.75 ft.³

Pressure 27.8 inches Hg.

Temperature 19.25°C.

Total lb. moles of off gas 0.325

Gas Analysis

Compound	Mole %	Moles	lb. atoms carbon	lb. atoms oxygen	lb. atoms hydrogen
Carbon dioxide	0.40	0.00130	0.00130	0.00260	-
Carbon monoxide	0.84	0.00273	0.00273	0.00273	-
Unsats.	0.42	0.00137	0.00274	-	0.00548
Butane	2.80	0.00912	0.03648	-	0.09120
Oxygen	1.25	0.00407	-	0.00814	-
Nitrogen	94.29	0.30650	-	-	-
Total	100.00	0.32509	0.04325	0.01347	0.09668

TABLE A-5

Liquid Product Work-up for Run A-3

Component	Mol. Wt.	Mole %	Comp. Wt.	Mole Fract.	Moles	lb. atoms carbon	lb. atoms oxygen	lb. atoms hydrogen
Methyl ethyl ketone	72.10	0.22	0.158620	0.008188	0.000394	0.001576	0.000394	0.003153
Acetone	58.08	0.02	0.016160	0.000834	0.000036	0.000108	0.000036	0.000216
Other ketones	86.13	0.14	0.120582	0.006224	0.000251	0.001255	0.000251	0.002510
Ethanol	46.07	0.06	0.027642	0.001427	0.000107	0.000214	0.000107	0.000642
Methanol	32.04	2.86	0.916344	0.047302	0.005214	0.005214	0.005214	0.020856
C ₃ & higher alcohols	60.09	0.70	0.420630	0.021713	0.001254	0.003762	0.001254	0.012032
Acetaldehyde	44.05	0.78	0.343590	0.017736	0.001397	0.002794	0.001397	0.005588
Formaldehyde	30.03	0.92	0.276276	0.014261	0.001648	0.001648	0.001648	0.003296
Carbon dioxide	44.01	0.14	0.061614	0.003181	0.000251	0.000251	0.000502	-
Oxygen	32.00	0.08	0.025600	0.001321	0.000143	-	0.000286	-
Carbon monoxide	28.01	0.52	0.145652	0.007519	0.000931	0.000931	0.000931	-
Water	18.02	93.56	16.859512	0.870293	0.167587	-	-	-
Total	-	100.00	19.372222	0.999999	0.179123	0.017753	0.012020	0.048293

Continuous Analyzers

The concentration of oxygen and carbon dioxide in the reactor product could be measured continuously by continuous analyzers on the product gas stream. One recorder was used for the two analyzers so that, in fact, only one or the other concentration was measured at a time. Normally the oxygen analysis was taken most of the time with only "spot checks" on the carbon dioxide concentration.

Oxygen Analyzer

The oxygen analyzer used was a Beckman F-3 oxygen analyzer which determines the concentration by measuring the paramagnetic susceptibility of the gas stream. The analyzer required calibration prior to each run.

Calibration

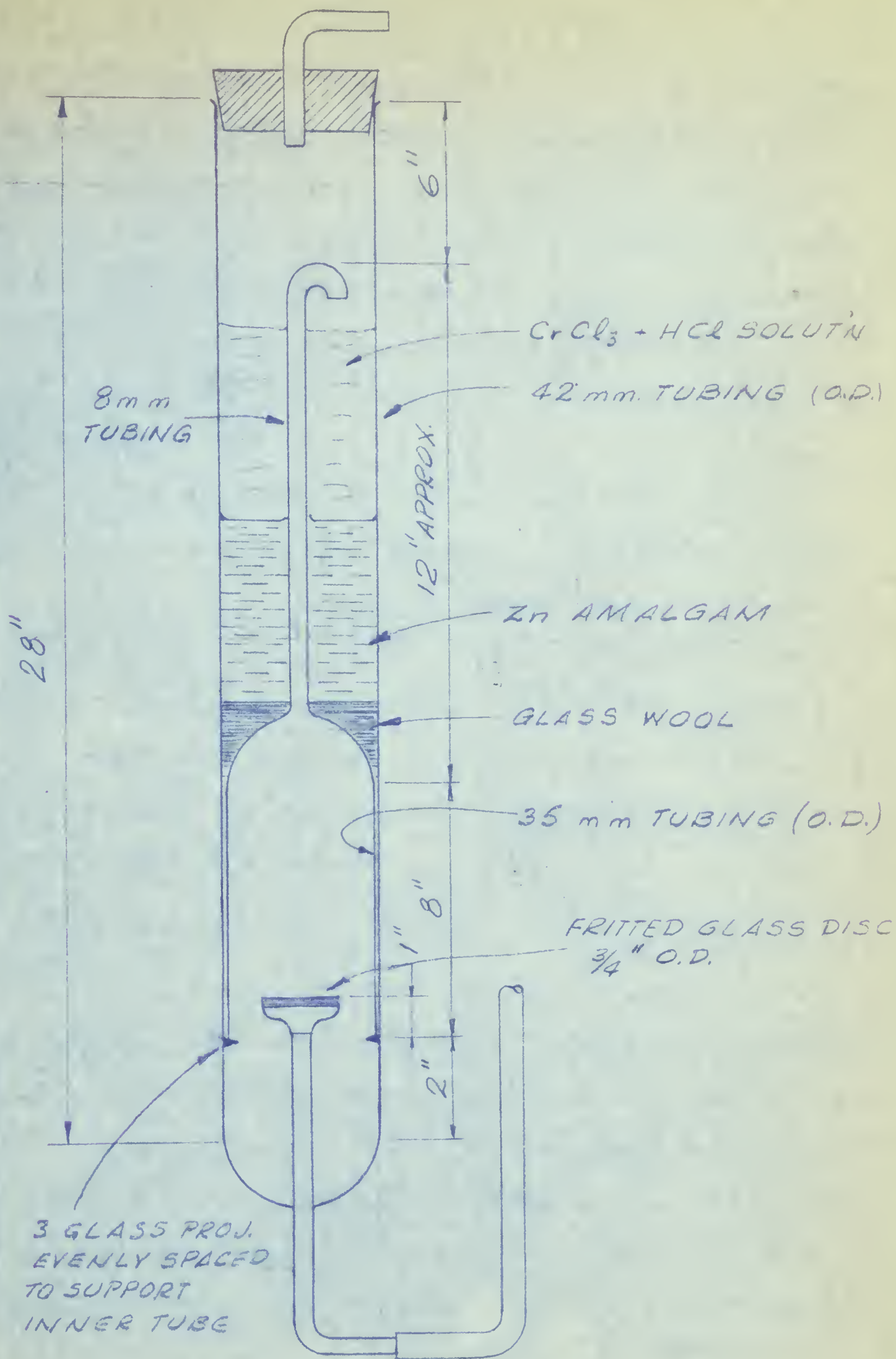
The oxygen analyzer was calibrated using an oxygen free stream of nitrogen for the zero adjustment and air as a gas of known oxygen concentration for the span adjustment. Oxygen free nitrogen was obtained by bubbling commercial nitrogen, of low oxygen concentration,

through a CrCl_3 and HCl solution. The solution was regenerated by passing over a zinc amalgam catalyst. The production of an oxygen free gas stream and the solution regeneration was carried out in the apparatus shown as Figure A-3. The chromus chloride solution was 0.5 M Cr Cl_3 in 1.0 M HCl . The zinc amalgam was prepared by: 300 gms of 30 mesh zinc was cleaned in HNO_3 until all the dark surface was gone. Approximately 1.0 gms of $\text{Hg}(\text{NO}_3)_2$ was added to the solution (to make a 0.2% amalgam). After the mercury had plated out the zinc amalgam was washed, dried and added to the apparatus.

Carbon Dioxide Analyzer

The continuous carbon dioxide analyzer was of the type described by Maxon and Johnson (13). The carbon dioxide containing gas was bubbled through a solution of sodium hydroxide. The carbon dioxide and water formed bicarbonate ions and hydrogen ions, in an equilibrium position dependent on the partial pressure of the carbon dioxide in the gas phase. The position of equilibrium could be measured by the hydrogen ion concentration in the solution. The hydrogen ion concentration was determined by a photometric measurement of the red colour of phenol red.

FIGURE A-3



APPARATUS FOR PURIFICATION OF
GAS CONTAINING OXYGEN

Light from a constant source was filtered through an Evelyn filter No. 565 which transmitted only the band of light that would be absorbed by the red colour of the phenol red indicator in the equilibrium solution. The light transmitted through the solution was measured by a photoelectric cell. The output of this cell gave an indication of the amount of carbon dioxide in the gas phase.

The analyzer is said to have a standard deviation of 2 parts per hundred from 0.06 to 12% carbon dioxide. However, in this study the instrument was only used as an indication of the carbon dioxide level in the gas and not for final measurement. Further development work would have been necessary to get the accuracy stated above. Orsat analyses were used as the basis for material balances.

Heat Balances

During each of the test runs temperature measurements were taken throughout the reaction zone as a measure of the amount of reaction taking place. These "thermal histories" of the runs are presented in the body of this report. The temperature change along the reactor provides a means to calculate the rate of heat release.

In order for the temperature to increase enough heat must be produced to increase the gas temperature and to supply the heat transferred to the bath. Or

$$\frac{dQ}{dl} = wC_p \frac{dT}{dl} + Up(T - T_b)$$

The rate of heat release can be determined from the slope of the temperature curve and the difference between the gas temperature and the bath temperature. Table A-6 gives the heat release calculations from the composite "thermal history" for the constant flow series. The overall heat release was calculated by graphically integrating the area under the rate of heat release curve.

Overall Heat Transfer Coefficient

The overall heat transfer coefficient was calculated by conducting a series of runs heating a gas stream. The rate of temperature increase was used to calculate the heat transfer coefficient.

A heat balance gives:

$$wC_p dT = Up dl (T_b - T)$$

This can be rearranged to:

$$\frac{dT}{(T_b - T)} = \frac{Up}{wC_p} dl$$

or

TABLE A-6

Heat Release

Constant Flow Series

ΔL	$\Delta T/\Delta L$	wC_p	$wC_p \Delta T/\Delta L$	$T-T_b$	U_p	$U_p(T-T_b)$	$\Delta Q/\Delta L$
0-1	-	3.08	-	-	1.95	-	-
1-2	-	3.08	-	-	1.95	-	-
2-3	-	3.08	-	-	1.95	-	-
3-4	-	3.08	-	-	1.95	-	-
4-5	-	3.08	-	-	1.95	-	-
5-6	1.0	3.08	3.08	0.5	1.95	1.0	4.1
6-7	1.0	3.08	3.08	1.5	1.95	2.9	6.0
7-8	2.0	3.08	6.16	3.0	1.95	5.9	12.1
8-9	2.5	3.08	7.71	5.0	1.95	9.7	17.4
9-10	3.0	3.08	9.27	8.0	1.95	15.6	24.9
10-11	4.0	3.08	12.3	11.0	1.95	21.4	33.7
11-12	5.5	3.08	16.9	16.0	1.95	31.1	48.0
12-13	9.0	3.08	27.7	22.0	1.95	42.9	70.6
13-14	16.0	3.08	49.4	34.0	1.95	66.1	115.5
14-15	35.0	3.08	108.0	51.0	1.95	99.4	207.4
15-15.4	152.0	3.08	468.0	120.0	1.95	234.0	702.0
15.4-16	100.0	3.08	308.0	175.0	1.95	341.0	32.0
16-17	-64.0	3.08	-197.0	90.0	1.95	175.0	-
17-18	-24.0	3.08	-74.2	52.0	1.95	101.0	27.0
18-19	-13.0	3.08	-40.1	34.0	1.95	66.2	26.1
19-20	-8.0	3.08	-24.6	25.0	1.95	48.7	24.1
20-21	-6.0	3.08	-18.5	18.0	1.95	35.1	16.1
21-22	-5.0	3.08	-15.4	12.0	1.95	23.4	8.0
22-23	-3.5	3.08	-10.8	8.0	1.95	15.6	4.8
23-24	-2.5	3.08	-7.7	5.0	1.95	9.7	2.0
24-25	-1.5	3.08	-4.6	3.0	1.95	5.9	1.3
25-26	-1.0	3.08	-3.1	2.0	1.95	3.9	0.8
26-27	-0.5	3.08	-1.5	1.0	1.95	2.0	0.5
27-28	-0.5	3.08	-1.5	0.5	1.95	1.0	-
28-29	-0.25	3.08	-0.77	0.25	1.95	0.5	-
29-30	-	3.08	-	-	1.95	-	-

$$-d\ln(T_b - T) = \frac{U_p}{wC_p} dl.$$

When $\ln(T_b - T)$ was plotted against the reactor length the slope of the curve is $-\frac{U_p}{wC_p}$. U could then be calculated. Experimental runs were made at three gas flow rates. The results of these runs are shown in Table A-7. The data are plotted in Figure A-4. The slopes of the lines were measured and the overall heat transfer coefficients calculated. The heat transfer coefficients for various flow rates are presented as Figure A-5.

Calculated Heat Release

The overall heat release during the run can be calculated from the heats of formation of the reactor feed and product components. These calculations were carried out on the constant flow series of reactions.

Heats of formation of the feed and product compounds are shown in Table A-8. The enthalpy of the various compounds at 725°F. is shown in Table A-9. Table A-10 shows the enthalpy of the reaction products and Table A-11 shows the enthalpy of the feed.

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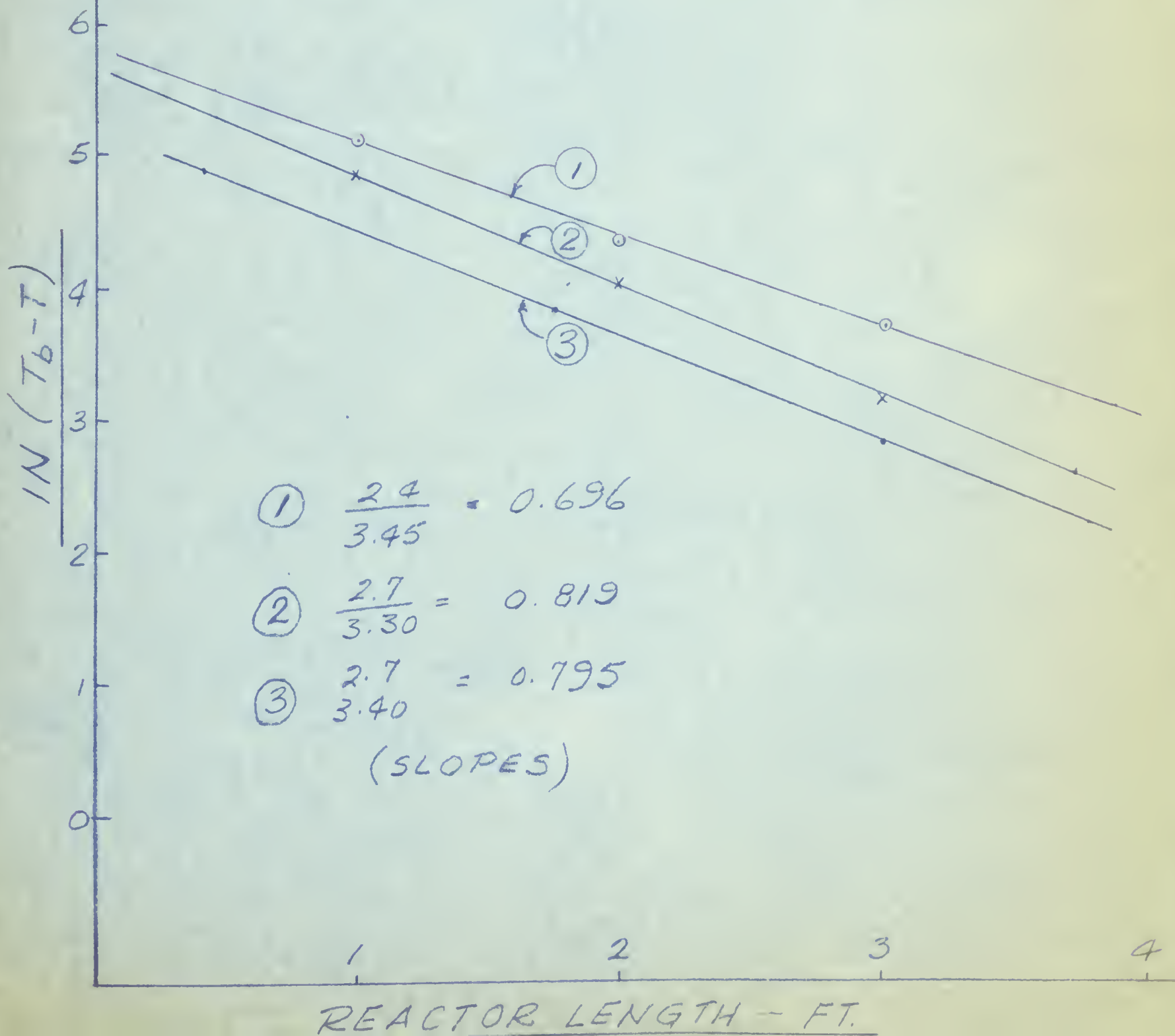
TABLE A-7

Heat Transfer Coefficient

Flow Rate								
9.63 lb./hr.			6.91 lb./hr.			3.80 lb./hr.		
L. ft.	$T_b - T_{b_{OF}}$	$\ln(T_b - T)$	L. ft.	$T_b - T_{b_{OF}}$	$\ln(T_b - T)$	L. ft.	$T_b - T_{b_{OF}}$	$\ln(T_b - T)$
0.0	235	5.46	0.0	187	5.23	0.5	68	4.22
1.0	167	5.11	1.0	130	4.86	1.75	47	3.85
2.0	80	4.38	2.0	57	4.04	3.0	17	2.83
3.0	41	3.71	3.0	24	3.18	-	-	-

FIGURE A-4

HEAT TRANSFER
MEASUREMENT



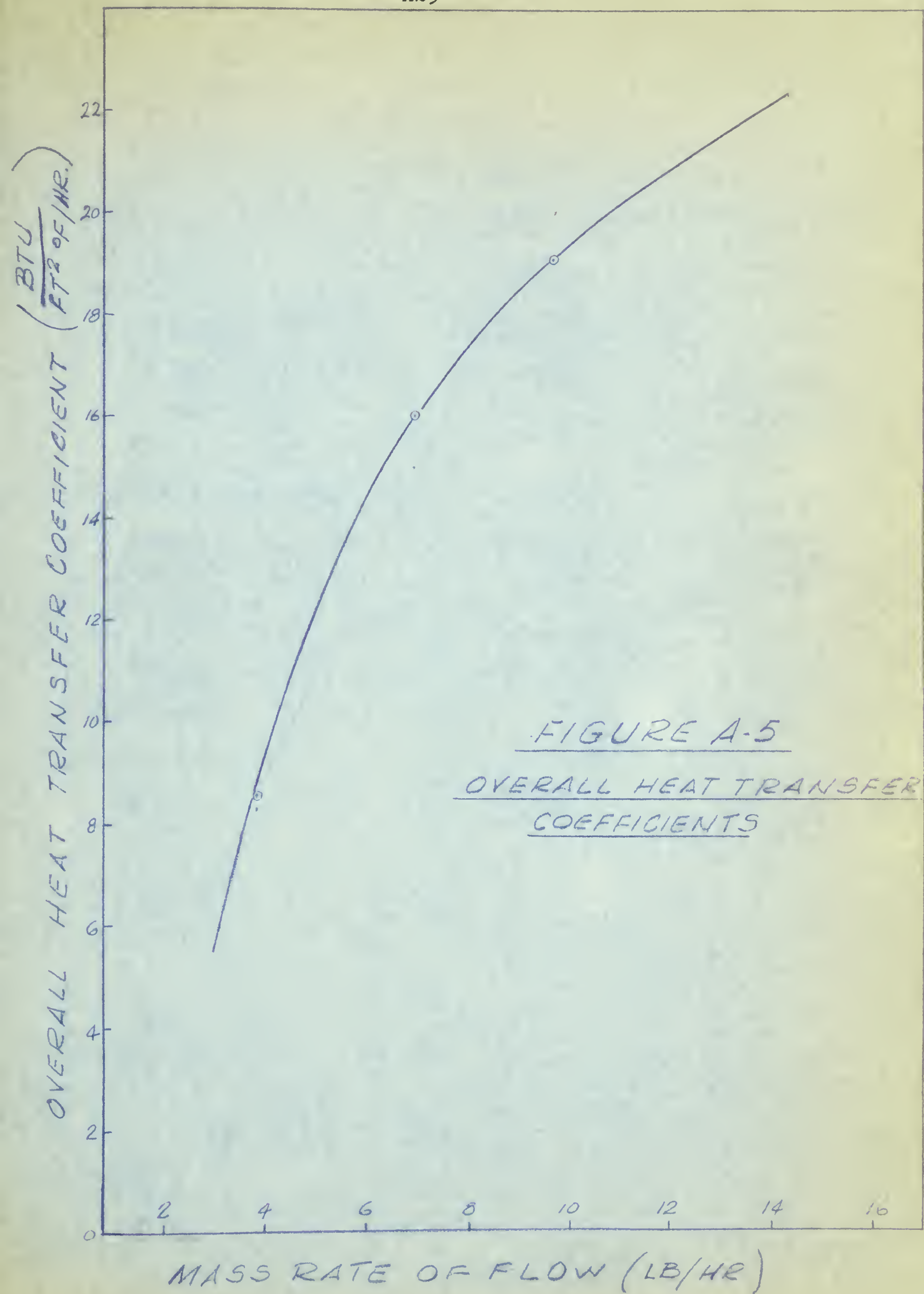


TABLE A-8

Heats of Formation (10)

	K.cal./gm. mol.	B.T.U./lb.mol. $\times 10^3$
Butane	- 29.812	- 53.662
Ethylene	12.496	22.493
Carbon Monoxide	- 26.416	- 47.549
Carbon Dioxide	- 94.052	-169.294
Oxygen	-	-
Methyl ethyl ketone (14)	- 56.28	101.304
Acetone	- 51.79	- 93.222
Diethyl ketone _{liq.}	- 73.8	-132.84
Ethanol	- 52.23	- 94.014
Methanol	- 48.08	- 86.544
Propanol	- 61.17	-110.106
Acetaldehyde	- 39.72	- 71.496
Formaldehyde	- 28.29	- 50.922
Nitrogen	-	-

TABLE A-9

Enthalpy of Feed and Products

B.T.U./lb. mole

Feed

Inlet Temperature 725°F.

Component	H ₇₂₅	H ₇₇	Δ H
Nitrogen	4,895.5	312.2	4,583.3
Oxygen	5,203.5	315.1	4,888.4
Butane	23,027.5	1,030.0	21,997.5

Products

Outlet Temperature 725°F.

Component	H ₇₂₅	H ₇₇	Δ H
Butane	23,027.5	1,030.0	21,997.5
Ethylene	9,866.0	454.0	9,412.0
Carbon Monoxide	4,929.0	313.3	4,615.7
Carbon Dioxide	7,147.9	392.2	6,755.7
Oxygen	5,203.5	315.1	4,888.4
Methyl ethyl ketone	-	-	20,550.0
Acetone	17,337.5	799.8	16,537.7
Diethyl ketone	-	-	41,665.0
Ethanol	15,855.0	772.2	15,072.8
Methanol	9,613.8	473.4	9,140.4
Propanol	20,792.5	925.0	19,867.5
Acetaldehyde	11,990.0	572.8	11,417.2
Formaldehyde	6,990.4	376.1	6,614.3
Nitrogen	4,895.5	312.2	4,583.3

TABLE A-10

Enthalpy of Reaction Products B.T.U.

Component	lb. moles $\Delta H_{(725-77)} \Delta H_f$	ΔH
Butane	(0.00912) (21,997.5 - 53,662) = -	288.8
Ethylene	(0.00137) (9,412 + 22,493) = +	43.7
Carbon Monoxide	(0.003661) (4,615.7 - 47,549) = -	155.0
Carbon Dioxide	(0.001551) (6,755.7 -169,294) = -	252.1
Oxygen	(0.004213) (4,888.4 -) = +	20.6
Methyl ethyl ketone	(0.000394) (20,550 - 101,304) = -	31.8
Acetone	(0.000036) (16,537.7 -93,222) = -	2.8
Diethyl ketone	(0.000251) (41,665 - 132,840) = -	22.9
Ethanol	(0.000107) (15,072.8 -94,014) = -	8.5
Methanol	(0.005214) (9,140.4 -86,544) = -	403.6
Propanol	(0.001254) (19,867.5 -110,106) = -	113.2
Acetaldehyde	(0.001397) (11,417.2 -71,496) = -	83.9
Formaldehyde	(0.001648) (6,614.3 - 50,922) = -	73.0
Nitrogen	(0.3085) (4,583.3 -) = +	1,413.9
Total		+ 42.6

TABLE A-11

Enthalpy of Feed B.T.U.

Component	lb. moles	$\Delta H_{(725-77)}$	ΔH_f	ΔH
Nitrogen	(0.3085)	(4,583	-)	= 1,414
Oxygen	(0.01345)	(4,888	-)	= 65.7
Butane	(0.0140)	(21,998 - 59,662)	= -	527.3
Total				+ 952.4

$$\text{Heat Release} = 42.6 - 952.4$$

$$= -909.8 \text{ B.T.U.}$$

Duration of Run 51.84 Minutes

Rate of Heat Release -1,050 B.T.U./hr.

TEST PROCEDURE

Check List for Experimental Runs

Prior to each Run

1. Compress nitrogen-oxygen supply.
2. Fill butane reservoir.
3. Prepare ice cubes from distilled water.

Night before each Run

1. Reactor heat turned on.
 - a) Immersion heater to medium position.
 - b) One 2000 watt element at lowest position.
2. Turn oxygen analyzer on.
3. Turn cooling water on to the reactor bath condenser.

Morning before the Run

1. Turn heat to reactor on full.
2. Turn butane preheater on.
3. Turn water to butane preheater condenser on.
4. Calibrate oxygen analyzer.
5. Turn CO₂ analyzer heater circuit on.
6. Calibrate CO₂ analyzer.

Preparation for Experimental Run

1. Pressurize reactor bath to give desired temperature.
2. Place ice in thermocouple cold junction boxes.
3. Place ice in jacket around ice-pot.
4. Water turned on to off-gas quench and cooler exchangers.
5. Nitrogen-oxygen flow started.
6. Reactor pressure adjusted to the desired level.
7. Nitrogen-oxygen flow rate set.
8. Nitrogen-oxygen stream started through oxygen analyzer.
9. Butane storage pressurized.
10. Butane flow started.
11. Turn heating element on butane line on.
12. Water turned into the absorption column.
13. Butane flow adjusted to give desired rate.
14. Observe when a constant oxygen concentration is reached in the off-gas with the correct butane flow. When this is reached the test can begin.
15. Start water flow to absorption column
16. Start draining absorption column.

17. Blow ice-pot free of condensate.

Beginning of Run. (All done simultaneously)

1. Read liquid level in butane reservoir.
2. Close absorption column drain.
3. Read off-gas meter.
4. Start timer.
5. Read temperature of butane and off-gas.
6. Start flow to aldehyde scrubber.

During the Run.

1. Take spot samples of the off-gas.
2. Check the carbon dioxide composition.
3. Take temperature measurements along the reactor. Establish the location and magnitude of the temperature peak.
4. Turn water to absorption column off when the column was full.
5. Hold nitrogen-oxygen and butane flows constant.

Preparation of Conclusion of Run.

1. Start water flowing to absorption column.
2. Start draining absorption column into a previously weighed bottle.
3. Blow condensate from the ice-pot.
4. Turn aldehyde scrubber off.

Termination of Run.

1. Read level of butane in reservoir.
2. Close absorption column drain. (Column fully drained).
3. Read off-gas meter.
4. Turn timer off.
5. Read temperature of butane reservoir and off-gas.

After Completion of Run.

1. Turn off all heating circuits.
2. Turn off butane and nitrogen-oxygen flows.
3. Turn off water to condensers and exchangers.
4. Turn off analyzers.
5. Carry out orsat analyses on spot samples.

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